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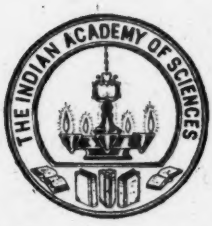

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THE STRUCTURE AND OPTICAL BEHAVIOUR OF PEARLS

By Sir C. V. Raman and D. Krishnamurti

(*Memoir No. 49 from the Raman Research Institute, Bangalore*)

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1. Introduction

The pearl holds a unique position amongst gems by reason of its natural beauty which needs no enhancement at the hands of the lapidary. It is also distinguished from the rest of them by the fact of its origin within the living body of a mollusc. For these reasons, it is a product of great and general interest. The aim of the present paper is to lay bare and express in the language of science the effects which pearls display and for which they are so highly admired.

The investigations here reported may be regarded as a sequel to a recent paper[1] by us in these *Proceedings* which concerned itself with iridescent shells. It was shown in that paper that the birefringence of nacre notably influences the spectral character of its iridescence. Further, it was shown that the discrete structure of the material results in characteristic diffusion phenomena which, no less than the iridescent reflections, make themselves evident in the observed optical behaviour of the shells. In view of the general similarity in nature of the material composing pearls and of the nacre in iridescent shells, it is to be expected that analogous effects would be observed in both cases. The spherical or nearly spherical shape of a pearl has however to be considered in this connection. Further, neither the structure of the material nor the nature of the stratifications is necessarily identical in the two cases. In the present paper, observations are presented bearing on these questions. The most noteworthy outcome of the investigation is to show that the diffusive properties of the material composing pearls play a major role, which is indeed no less important than the reflection of light by the stratifications, in making pearls the beautiful objects that they are.

2. The Birefringence of Pearls

It is well known that in the production of cultured pearls, a sphere of extraneous material (usually mother-of-pearl) is inserted within the mollusc, as a result of which, it deposits a whole series of layers in the course of years around the nucleus thus provided. By cutting a cultured pearl in two

halves, it is easy to remove the nucleus and obtain two hemispherical shells of the deposited material. These shells are in a very useful form for a study of the optical characters of the substance composing pearls.

Placing such a hemispherical shell between crossed polaroids and viewing it normally along its axis through a magnifying lens against a source of light, one observes an interference figure (see Fig. 15 in Plate XVIII) which is very similar to the conoscopic figure of a plate of a biaxial crystal seen under the polarising microscope. It is remarkable that such a figure is observed in *parallel light* in the present case. The explanation of it is the hemispherical shape of the shell coupled with the fact that its optic orientation everywhere follows the curvature of the surface. Hence, when traversed by a parallel beam of light, the interference figure is localised at or near the curved surface of the shell. If the hemisphere is rotated round its axis, the isochromatic lines in the figure are observed to rotate with it, while the isogyres pass through a cycle of changes. If, on the other hand, the hemispherical shell is rotated around a diameter, the entire pattern drifts along the surface of the shell but remains substantially unaltered.

Another simple and effective way of exhibiting the birefringence is to grind one of the hemispherical shells cut from a cultural pearl to a flat surface on both sides and to mount the plate thus obtained in canada balsam between glass coverslips. Since the stratifications in the material are curved, a specimen thus prepared and mounted reflects light like a spherical shell. However, when held up against a lighted window, it becomes evident that the plate has a circular bevelled edge where the original spherical surface meets the parallel plane faces. This bevelled edge acts like a circular prism, and since the material is doubly refracting, two concentric rings of light are seen around a source of light when the latter is viewed through the plate (see Fig. 1, Plate XV). On tilting the specimen, the two circles become eccentric with respect to each other (see Fig. 3, in Plate XV). On further tilt, both the rings of light become elliptic, the outer one much more so; the two ellipses touch each other at one end of the major axis and are widely separated at the other end (see Fig. 5, Plate XV). At such oblique settings the rings also exhibit distinct colours due to dispersion. That these effects arise from the birefringence of the material is confirmed by viewing the rings of light through a polaroid. It is then noticed that the rings are extinguished in certain regions which shift around as the polaroid is rotated (see Figs. 2, 4 and 6 in Plate XV). In the case in which the source of light is viewed normally through the plate, the rings are extinguished at the ends of two diameters which are mutually perpendicular to each other.

3. The Structure of the Pearly Layers

The shells of the bivalves[2] exhibit conoscopic figures closely resembling that reproduced as Fig. 15 in Plate XVIII. It follows that the orientation of the aragonite crystallites is very similar in the two cases. In other words, the crystallites in pearls have their *c*-axes more or less exactly normal to the laminations, while their *a* and *b* axes also have fairly defined orientations in the plane of the laminations. This is confirmed by X-ray diffraction studies, all that is necessary being to send a fine pencil of X-rays along the axis of the hemispherical shell and to record the results on a flat film. Two such photographs recorded at this Institute by Mr. A. Jayaraman are reproduced as Figs. 7 and 8 in Plate XVI. The former was obtained with the filtered X-radiation from a copper target and the latter with unfiltered molybdenum radiation. In both records, we notice that the bright arcs have a finite spread, thereby indicating that the orientations of the *a* and *b* axes in the plane of the stratifications have a tolerably large range of variation. It may likewise be assumed that the direction of the *c*-axis is also sensibly variable, as has been established by X-ray methods[3] in the case of the bivalve shells. Comparison of Fig. 8 with the figures reproduced in the papers of Rama Swamy quoted show that the fluctuations in the orientation of the *a* and *b* axes are of the same order of magnitude in the two cases.

When a bright source of light is viewed normally through a thin plate of an iridescent shell having its faces parallel to the stratifications, a characteristic diffusion halo is observed; for the bivalves, this consists of a diffuse central spot overlying the source and two other diffuse spots lying one on either side of it.[1] The observation indicates that the aragonite crystallites are arranged in parallel rows along the lines of growth of the shell; the spacing of the rows calculated from the separation of the diffuse spots agrees with that directly observed with thin sections examined under the microscope.[2] If the material in cultured pearls had a similar structure, we should expect to be able to observe it when thin layers are examined under the microscope and also to see similar diffusion haloes. These anticipations are to some extent supported by the results of observation. We do indeed find that thin plates of the material under a microscope exhibit a fibrous structure in the plane of the laminations. We are also able to observe in some cases, diffusion haloes similar to those of the bivalve shells (see Fig. 13 in Plate XVIII). On the other hand, in other cases, a different form of diffusion halo is observed, consisting of a pattern of six diffuse spots arranged in the form of a hexagon and surrounding the central diffuse spot; two of these spots at the end of a diameter are brighter than

the rest (see Fig. 14 in Plate XVIII). In the deposition of pearly material round a spherical nucleus, it is difficult to see why any particular direction on the surface should be favoured. It is therefore a little surprising that parallel rows of crystals, as in bivalve shells, are found in many cases. *Per contra*, it is not surprising that in other cases a halo indicative of a grouping of the crystallites in hexagonal order in the plane of the laminations is observed.

4. THE OPTICAL BEHAVIOUR OF PEARLS

Some General Remarks.—The appearance which any object presents to an observer is determined by the manner in which it is illuminated and by the particular way in which the light falling on the object is returned to the eye. Consider, for example, a case in which the object under examination is a polished metallic sphere held at some distance from an open window and viewed by the observer against a black background. The more perfectly polished the sphere is, the less would be the intensity of the light scattered by its surface. All that the observer would see in these circumstances is a well-defined image of the lighted window formed by reflection at the convex surface, while the sphere itself would hardly be visible. It is clear from this example that the possession of a high reflecting power by a spherical body would not by itself make it appear an attractive object.

The reflection of light by a pearl, however, occurs not solely or even principally at its surface. A whole series of spherical laminations participate, and since the material is optically heterogeneous, the reflections at the successive layers would be accompanied by a strong diffusion which would appear spread out over a range of solid angles, instead of forming a well-defined image of the luminous object. Hence, unless the source of light be of very small angular dimensions, its reflected image would be overlaid by diffuse light, and hence prevented from its being readily observed; *per contra*, the illusion would be created that the pearl is itself a lustrous and brilliant object. It is thus evident that the diffusion of light in directions approximating to that of regular reflection contributes notably towards making the pearl an attractive gem. The diffusion in other directions also plays an important role, as will appear later.

The Reflection-Diffraction Spectra.—With our earlier paper, we reproduced several photographs of the reflection-diffraction spectra of iridescent shells. These were recorded by allowing a narrow pencil of light to fall on the surface of a shell and receiving the reflected and diffused light on a photographic film held a few centimetres away. The photographs show very clearly that the diffraction of light by the corrugations at the external boundary

and the reflection of light by the internal stratifications form a single coherent series of spectra, the iridescence usually appearing as the last of the series on one side. A similar phenomenon can also be observed with pearls when a magnifying lens is focussed on the image of a distant source of light formed by reflection at the surface of the pearl. A series of spectra are then seen in focus whose separation depends on the angle at which the stratifications meet the surface; if they were strictly parallel to the surface, the spectra would all overlap and we would observe only a single coloured image of the source. More generally, however, the spectra are seen clearly separated.

The Diffusion-Halo of Reflection.—Surrounding the reflected image of the source (or the whole group of reflection-diffraction spectra) is observed a phenomenon which may be designated as the diffusion-halo of reflection. The structure of this halo varies to some extent from specimen to specimen. It is most clearly seen when the external surface is truly spherical and the stratifications are parallel to the surface, so that we observe only a single image of the source formed by reflection and exhibiting the characteristic iridescence. Through this image runs a straight band of light terminated by two diffuse spots and exhibiting over its length approximately the same colour as that of the iridescent reflection. This band is encircled by two coloured arcs lying on either side of it and exhibiting a tint complementary to that of the iridescence. The obvious analogy between this and the diffusion haloes by transmitted light reproduced as Figs. 13 and 14 in Plate XVIII makes it clear that its origin is to be sought for in the discrete structure of the stratifications reflecting the light. The reason why the reflection halo exhibits complementary colours in the different parts of it is not difficult to fathom. The most prominent features of the halo are those due to light selectively reflected and diffracted by the upper layers of the stratifications and hence exhibiting the characteristic colour of the iridescence. The rest of the light thus filtered out would penetrate deeper into the stratifications and would be returned by diffusion, thereby appearing spread out over a wider range of angles, and this would exhibit the complementary colour.

Some Illustrative Examples.—Figs. 9 and 10 in Plate XVII illustrate some of the observations set out in this and the preceding section. They are photographs respectively of a natural and of a cultured pearl illuminated in each case by two filament lamps set one on either side of the pearl. The cultured pearl appearing in Fig. 10 was a rather perfect specimen of spherical shape. On the upper right of that picture can be seen a small bright spot being the coloured image of the source formed by reflection and this appears surrounded by an extended area of diffuse radiation. Lower down in the

picture can be seen the image of the second lamp surrounded by a rather complicated pattern of diffused light.

The natural pearl which appears in Fig. 9, though larger than the cultured pearls in our possession and far more expensive, had a rather irregular shape, and the optical effects exhibited by it were rather irregular. In the patch of light seen in the upper right hand side of the picture, the long streak and the diffuse spot separated from it record the reflection-diffraction spectrum exhibited by that part of the surface. These features appear surrounded by a strong patch of diffuse light. In the lower part of the same picture, effects of the same general nature due to the second source of light appear.

The Whispering Gallery Effect.—The photographs reproduced as Figs. 9 and 10 in Plate XVII were recorded with the pearls placed on a sheet of black glass and in a dark room with blackened walls. Nevertheless the whole of the pearl shows up quite clearly. Not only are the spherical margins clearly seen, but they are actually somewhat brighter than the central regions of the pearl. Closely connected with the explanation of these facts is the very remarkable phenomenon illustrated in Figs. 11 and 12 of Plate XVII, recorded respectively with a cultured and a natural pearl. In Fig. 11 the pearl was illuminated tangentially on the side remote from that in which it was observed. Nevertheless it will be seen that the rear face is seen brilliantly illumined, the edges in particular being very bright. In Fig. 12, the pearl was illuminated at a part of the surface a little to the rear of that visible in the photograph. Nevertheless it can be seen that the entire periphery of the sphere appears lit up, the part on the right much more so.

The explanation of these effects is evidently related to the phenomenon of the lateral or transverse diffusion of light in nacre described and illustrated in a paper[4] published in these *Proceedings* twenty years ago. It was there shown that light penetrates nacre by diffusion through far greater distances parallel to the laminations than perpendicular to them. It is clear that a similar effect is operative also in the case of pearls. Light diffuses in directions parallel to the spherical laminations through considerable distances with relatively little loss, thereby enabling the pearl to be lit up and become visible in areas where no light falls directly.

The Spectral Character of the Iridescence.—Owing to the spherical shape of the pearls and the relatively small sizes available, the recording of the spectrum of iridescence presents some difficulties. The angle of incidence of the light would vary rapidly from point to point on the surface of the pearl and so also the spectral character of the iridescence. Hence it would be necessary to severely restrict the aperture of the incident beam and of the

reflected beam as well. The iridescence exhibited by pearls varies considerably in its hue and saturation from specimen to specimen. The pearls taken up for examination were naturally those that exhibited the most vivid colours. Even in their cases, however, the results were rather disappointing. Complex spectra exhibiting a great many maxima of illumination, some stronger than the rest, were recorded. Further, the spectrum also showed large variations in different areas of the same specimen. See Figs. 16 (*a*), (*b*), (*c*) and (*d*) in Plate XIX recorded with a cultured pearl and Figs. 17 (*a*), (*b*) and (*c*) in Plate XX recorded with a natural pearl. These were obtained with the light beam incident normally on the specimen.

It would seem from these facts that the stratifications in pearl are somewhat different in nature from those in nacre. It appears not improbable that they consist of distinct groups of layers, each having a separate spacing and not a single continuous sequence. However, this is only a surmise which has to be tested out by further study of different specimens and a careful comparison with the nacre from the same species of mollusc.

Effect of Birefringence on the Iridescence.—In spite of the complicated nature of the spectra, it has been found possible to establish their bifurcation at oblique incidences due to birefringence, as has already been done by us with nacre. Figs. 16 (*e*), (*f*) and (*g*) are the spectra of a cultured pearl recorded respectively with vibrations perpendicular to the plane of incidence, with vibrations in the plane of incidence and with the vibrations unpolarised. The shift of the bands as between Figs. 16 (*e*) and 16 (*f*) is readily seen, while Fig. 16 (*g*) is clearly a superposition of both. Figs. 17 (*d*), (*e*) and (*f*) are similar records obtained with a natural pearl and analogous effects are there noticed.

Figs. 16 (*h*), (*k*) and (*l*) in Plate XIX obtained with a cultured pearl exhibit an interesting effect. They were recorded in circumstances similar to those of Figs. 16 (*e*), (*f*) and (*g*) but with the beam incident on the surface of the pearl at an angle of about 60°. As in all other cases, the sphere was kept immersed in liquid paraffin to minimise disturbing effects at the external surface. It will be seen that the iridescence is almost completely polarised with its vibration direction perpendicular to the plane of incidence. Surprisingly enough, this effect was observed to persist over a wide range of angles of incidence.

Transmission Spectra.—Fig. 18 in Plate XX shows the spectra of the light transmitted by the hemispherical shell obtained from a cultured pearl, the incidence being normal in (*a*), (*b*) and (*c*) and a few degrees away from normal in (*d*), (*e*) and (*f*). The three spectra in each group were recorded

respectively with light having its vibration direction perpendicular to the plane of incidence, the same lying in the plane of incidence and with the vibrations unpolarised. It will be noticed from the pictures that there is a noteworthy extinction of the component in the plane of incidence at oblique incidences, a phenomenon clearly analogous to that already noticed by us in the case of nacre.

5. SUMMARY

The paper embodies a study of the structure of the material composing pearls and of the optical effects which they display. The following topics are dealt with: (1) Birefringence, (2) X-ray-diffraction patterns, (3) The reflection-diffraction spectra, (4) The diffusion haloes of reflection and transmission, (5) The whispering-gallery effect, (6) The spectral character of iridescence and the influence of birefringence thereon, (7) The transmission spectra. The most noteworthy result of the investigation is to show that the diffusive properties of nacre play a major role no less important than that of the reflection by its stratifications in the optics of pearls.

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A detailed account of the origin and structure of pearls will be found in F. Haas' book "Bau Und Bildung Der Perlen", Leipzig, 1931. See also W. J. Schmidt's "Die Bausteine Des Tierkorpers", Bonn (1924), pages 166–169.

The culturing of pearls is an important Japanese industry and several laboratories in that country are at present investigating its problems and have published papers dealing with various aspects of the subject which are collected together in Bulletin No. 1 of the Nippon Institute for Scientific Research on Pearls (1953). The following papers are those referred to in the text.

1. Raman, C. V. and Krishnamurti, D. .. *Proc. Ind. Acad. Sci.*, 1954, **39A**, 1.
2. Rajagopalan, V. S. .. *Ibid.*, 1936, **3A**, 572.
3. Rama Swamy, S. .. *Ibid.*, 1935, **1A**, 871; **2A**, 345.
4. Raman, C. V. .. *Ibid.*, 1935, **1A**, 859.

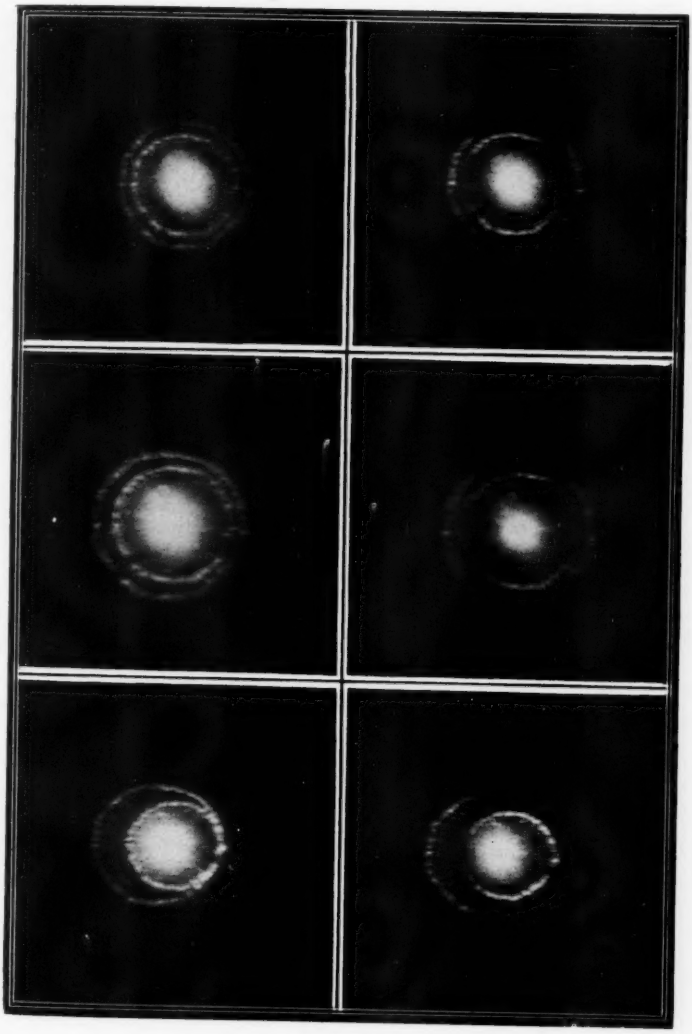

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

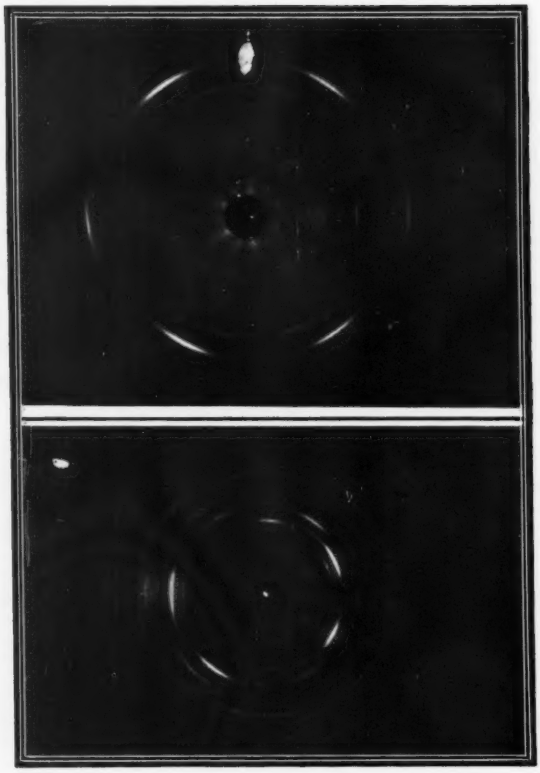

FIG. 7

FIG. 8

FIG. 9

FIG. 10

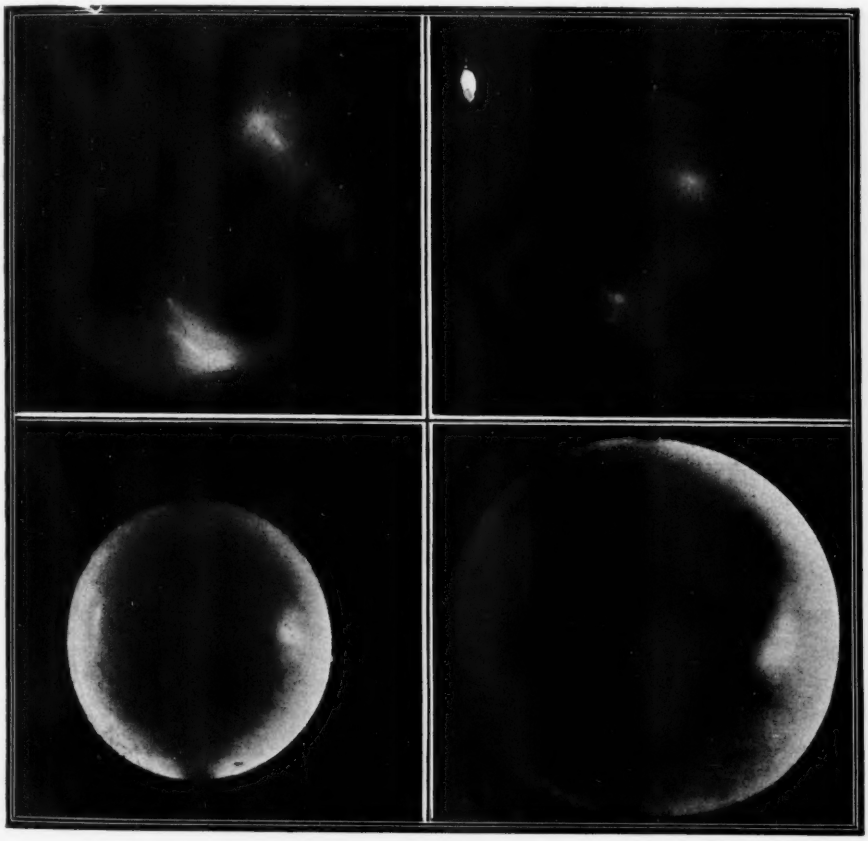

FIG. 11

FIG. 12

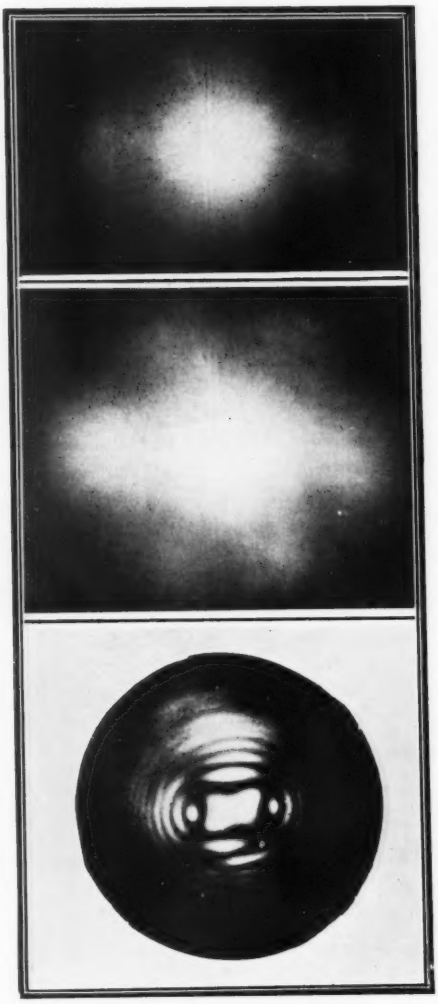

FIG. 13

FIG. 14

FIG. 15

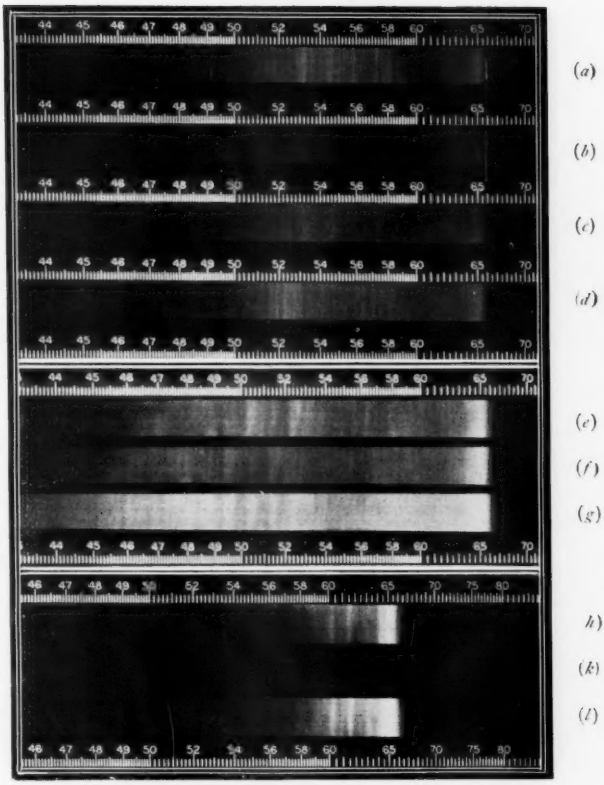

FIG. 16

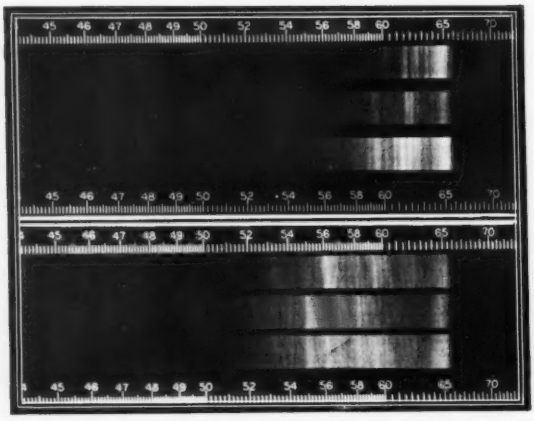
45 46 47 48 49 50 52 54 56 58 60 65 70
(a)
(b)
(c)
(d)
(e)
(f)

FIG. 17

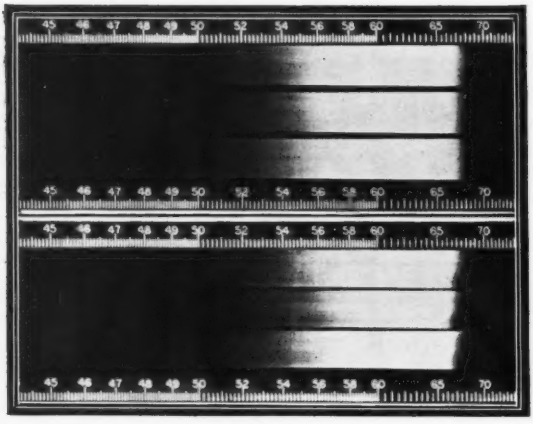
45 46 47 48 49 50 52 54 56 58 60 65 70
(a)
(b)
(c)
(d)
(e)
(f)

FIG. 18

PREFERRED ORIENTATION IN ROCKS AND ITS RELATION TO THEIR PHYSICAL PROPERTIES

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(From the Geology Department, Andhra University, Waltair)

Received November 11, 1953

(Communicated by Prof. C. Mahadevan)

1. Introduction

Structural petrology or petrofabrics deals with the systematic study of inter-relationships between the structure of rocks in the field and their textures as revealed in the laboratory. Such a study of rocks is important genetically because it gives an idea of the spacial physical data which go to form a complete vector picture of the make-up of the rock. Sanders and Schmidt (1938) have systematised this new method of study of the rock fabric by statistical determination of a pattern of orientation of crystallographic or other optical elements of the constituent minerals. Sanders, Fairbairn (1949), Knopf and Ingerson (1938), Bain (1936), Cloos (1946), Turner (1948), Riley (1947), Balk (1952), Saurindranath Sen (1949), Kar and Sirkar (1952) and Srirama Rao (1953) are amongst those who studied the fabric orientation of calcite in marble, and of quartz in quartzites and in granites, and came to certain conclusions.

In an earlier communication, the author (1953) determined the ultrasonic velocities in some quartzites and marbles from the members of the Pakhal formation of Warangal in Hyderabad State and granites of Archæn age, also from Hyderabad. It was then thought that valuable data concerning structure and tectonics of these formations are likely to emerge, if the results regarding sound velocities are correlated with the fabric orientation of certain index minerals contained in the rocks under investigation. Accordingly, a petrofabric determination of calcite and quartz, in the specimens already used for studies in ultrasonics, has been carried out and results are given in this paper.

2. Petrofabric Study of Rocks

Some important field observations and a detailed megascopic and microscopic examination of the rocks are given below:

Field observations

The quartzite is from Yellandulupadu in the Warangal District (Sheet No. 65 C/N.W.). The strike of the formation is N.W.-S.E. (130 ....1/80..) dipping 80° to S.W. It is flesh coloured and has a sub-vitreous lustre. It is very compact. Lineation is clearly visible in the hand specimen making an equal angle with the direction of strike and dip. Sheer joints are present, suggesting a deformation.

The granite is from Osmania University (Hyderabad) (Sheet No. 56 *k*/7). It has a trend N.N.W.-S.S.E. (..1/85....12) sloping S.W. at 85°. It is characteristically pink coloured. It is very hard and compact and has a pitted appearance. Lineation is not so prominent in the hand specimen.

The marble is from Manditog, North of Singareni Collieries (Warangal, Hyderabad) (Sheet No. 65 C/N.W.). Formations are having a strike of N.N.W.-S.S.E. (120 ....!/15....) dipping 15° to S.W. It is white in colour and has a pearly lustre. It is very compact and crystals of calcite and dolomite are clearly visible.

Microstructures

The deformation of rocks is further evidenced by their microstructures. The quartzite is equigranular and fine-grained. Most of the grains are round in shape, a few being elongated. Some of the quartz grains show brushy extinction. Most of the grains get extinct or appear with very nearly the same polarisation colour by slight rotation of the microscope stage thereby indicating a high degree of preferred orientation. There is ferruginous matter around some grains. A few mica flakes of irregular shape are seen. Trains of inclusions are observed, sometimes parallel to the length of the grains. The rock is made up essentially of quartz grains.

The granite is inequigranular and is medium to coarse grained, the grain size varying from 1 mm. to 6 mm. Felspar and quartz are the essential minerals while mica, hornblende, magnetite and zircon are the accessories. The felspar is of the perthetic variety. The model composition of the granite is as follows:

Quartz 32·5%, felspar 58·1%, mafic minerals 9·4%.

The marble is fine-grained and equigranular. Most of the grains are elongated. A large number of grains get extinct at more or less the same position of microscope stage indicating optical continuity and also a high degree of preferred orientation. The rock is essentially made up of calcite and dolomite.

Methods of study

The specimens for petrofabric study are oriented in the field with respect to structural directions such as strike and dip. Sections are cut perpendicular to strike direction in all the four cases for comparison, and in the case of quartzite a section perpendicular to dip is also taken in order to study the homogeneity with respect to preferred orientation. In all the cases, measurements were made on four axis universal stage for 150 to 400 grains to represent the result statistically. The co-ordinates of the poles of the optic axis with respect to two fixed directions of a microscope have been determined. The points were all plotted on a Schmidt net of 20 cm. equal area lower hemisphere projection and are all counted with a 1% circle.

Fabric results.—Preferred orientation of grains according to space lattice structure is expressed in orientation diagrams by the presence of localised

FIG. 1.

Petrofabric diagram of quartzite (Section cut perpendicular to dip) 400 quartz axes, 10-9-8-7-6-5-4-3-2-1 %.

areas, called maxima and arcuate zones, named girdles, within which the poles of the measured optic axes are densely concentrated. Figs. 1 and 2 represent the fabric orientation of quartz grains in quartzite. Fig. 3 represents the fabric orientation of quartz grains in granite. Fig. 4 represents the fabric orientation of calcite in marble.

400 poles of quartz grains of the quartzite from a section cut perpendicular to dip have been plotted in Fig. 1. There is concentration of points in definite areas. Girdles are formed along the periphery of the fabric diagram which coincides with the strike plane. The density diagram indicates a point maxima of 11% in a direction which is inclined to North by 45°. There is also a point maxima at the centre of the diagram which coincides with the dip direction. But here the concentration is only 7%.

FIG. 2.

Petrofabric diagram of quartzite (Section cut perpendicular to strike) 300 quartz axes, 11-10-9-8-7-6-5-4-3-2-1 %.

300 poles of quartz of the quartzite from a section cut perpendicular to strike have been plotted in Fig. 2. There is a definite concentration of points in some areas. Girdles have been formed at the periphery of the diagram which coincides with the dip plane. The density diagram shows a point maxima of 11% as in the previous case (Fig. 1) but in a direction inclined to North by about 35°. There is again a point maxima of 3% at the centre of the diagram which coincides with the strike direction.

150 poles of quartz grains from a section cut perpendicular to strike direction from a granite have been plotted in Fig. 3. Peripheral girdles are formed throughout the diagram. Contour lines are formed nearly parallel to the periphery of the diagram somewhat like concentric circles. Concentration is mostly in the direction of N.N.W.-S.S.E. which coincides with the dip direction. The maximum contour value is 5. The appearance

FIG. 3.

Petrofabric diagram of granite (Section cut perpendicular to strike) 150 quartz axes, 5-4-3-2-1 %.

of the many subsidiary maxima may be attributed to the fact that the section is not cut in a direction which is exactly perpendicular to dip direction but along one which is making a slight angle of 8°.

400 poles of calcite grains of marble from a section cut perpendicular to strike have been plotted in Fig. 4. Girdles are formed at the periphery which coincides with the dip plane. The density diagram shows a point

FIG. 4.

Petrofabric diagram of marble (Section cut perpendicular to strike) 400 calcite axes, 10–9–8–7–6–5–4–3–2–1 %.

maxima of 10% at the periphery in a direction which is making a slight angle with the North. The conspicuous absence of the maxima at the centre of the diagram and their clustering at the periphery indicates a preferred orientation in the dip direction but not along the strike direction.

3. DISCUSSION

Deformation in the rocks is very well understood by considering the symmetry of the fabric and the amount of the preferred orientation. The

most striking feature of the present investigation of quartzites, granites and marbles is that there are difinite maxima in the diagrams roughly coinciding with certain important directions.

Quartzite.—In both diagrams (Figs. 1 and 2) obtained from a study of the sections cut perpendicular to both strike and dip, the direction of elongation of grains is the same but the degree of preferred orientation varies. The similarity in patterns in both the diagrams may be explained by the fact that the major structural feature, namely the foliation or the plane of bedding is making an equal angle with the strike plane and the dip plane. It is possible that the direction of concentration of grains coincides with the plane of weakness in a rock. The grains of quartz have a characteristic directional orientation all being aligned with their maximum lengths in more or less one and the same direction. Further, there is lattice orientation as revealed by the marked concentration of the poles of quartz axes. Thus the quartzite under examination is a tectonite. Here 11% of grains are elongated in a direction which may be correlated to the plane of weakness or possibly to a plane of foliation. Peripheral girldes suggest a movement in the axial plane. A high degree of preferred orientation suggests that the rocks are very much deformed and the deformation has occurred only once. The almost homogeneous nature of the rock fabric also suggests that the deformation has not varied much in the two directions of the rock.

Granite.—In granites, the quartz orientation is studied. It is evident from Fig. 3 that 5% of quartz grains are elongated in the dip direction. The peripheral girdle indicates a movement along the plane of gneissosity. The presence of contours throughout the periphery of the diagram is rather significant. The fabric diagram obtained in this investigation is in general agreement with Cloo's (1946) diagram for Ellicott city granite. 5% of orientation in the dip direction which is probably perpendicular to the direction of lineation, indicates a movement along dip plane upwards.

Marble.—Carbonate minerals, Calcite and Dolomite, exhibit a high degree of deformation especially as they occur in marbles, crystalline limestones and dolometic limestones most of which are tectonites. Fig. 4 shows a preferred orientation of 9% of grains in the marble which suggests that the rock has undergone a strong deformation. Such a degree of preferred orientation is not uncommon in marbles. The diagram is in general agreement with that of previous workers. The conspicuous absence of clustering of points near the centre and concentration of 9% of grains near the periphery suggests that there is a preferred orientation in a plane containing dip. It is also possible that the direction of lineation may

coincide with the direction of movement along which the deformation took place.

4. CORRELATION OF FABRIC RESULTS WITH ULTRASONIC RESULTS

In an earlier paper by the author (1952), an interesting result connecting the granular texture with the transmission of sound in rocks has been reported. It was found that sound transmission in rocks is dependent upon particle size, closeness of packing and on the variation of mineralogical composition from grain to grain in the specimen. A petrofabric investigation of some of the rocks like quartzite and marble, now reveals a higher degree of preferred orientation of grains in definite areas, and in definite directions than what is revealed in granite. This observation may be correlated with the fact that quartzites and marbles transmit sound with ease and give intense diffraction patterns unlike granites. It is concluded from this that sound transmission also depends to some extent on the degree of preferred orientation; quartzites and marbles with preferred orientation ranging from 9 to 11% being such that they permit sound to go through more easily than granites which show preferred orientation of only 5%.

In another paper by the author (1953), the anisotropic behaviour of these rocks has been studied. It was concluded that in sections cut with reference to dip and strike directions, ultrasonic velocities remain more or less the same and the differences, if any, are only within the plausible experimental errors. It is interesting to note that the petrofabric investigation now carried out in quartzites shows that the same 11% of grains are elongated in one and the same direction, irrespective of whether the section is cut perpendicular to the plane containing strike or dip. This leads us to two important conclusions. The first is of a physical nature and relates to the fact that the preferred orientation of quartz grains is not the major contributing factor to the elastic isotropy or otherwise of the rocks but it is the structural deformation, if any, in the direction of dip, strike and so on. The second one is of a mineralogical nature and relates to the almost homogeneous nature of the fabric which suggests that the deformation of the rock has not been much variable in two directions. This is perhaps due to the monomineralic nature of the rock.

The results regarding ultrasonic velocity measurements in quartzites lead us to the conclusion that they are almost isotropic and it becomes at once clear that this is what one should expect if the equivalent deformation in both directions as observed from petrofabric studies is correlated with elastic-isotropic nature of the work.

5. Summary and Conclusion

The degree of preferred orientation of quatz grains in quartzite and granite, and that of calcite in marble is studied in the present investigation. 11% of the quartz grains in quartzite, 9% of calcite grains in marble and 5% of quartz grains in granite are elongated in definite directions indicating that the rocks have undergone a strong deformation. The homogeneity of the fabric in quartzites is studied by determining preferred orientation of quartz grains in two mutually perpendicular directions. The same 11% of preferred orientation in sections cut perpendicular to the plane containing strike and dip indicate a uniform deformation in both directions. In the present investigation, the petrofabric studies have been made in rocks, for which the elastic properties are studied and they suggest an interesting correlation. The degree of anisotropy is shown to be directly correlatable with the degree of deformation.

In conclusion, the author desires to express his grateful thanks to Professor C. Mahadevan for his kind interest and guidance.

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SYNTHESIS OF QUINOLIZINE DERIVATIVES

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Polycyclic structures incorporating the quinolizine ring system are present in berberine and related alkaloids. An ingenious method for the synthesis of such types of benzo- and dibenzoquinolizines was developed by Sugasawa and Sugimoto.[1] This consisted in the oxidation by alkaline ferricyanide of a quarternary salt formed between a β-aryl ethyl halide and a heterocyclic base, to the cyclic amide, followed by the cyclisation of the latter with phosphorous oxychloride to a quinolizinium halide. The method has been successfully applied for the synthesis of analogues of emetine.[2] However, only alkoxy substituted β-aryl ethyl halides and similarly substituted heterocyclic bases have so far been used in this method probably due to the belief that in the absence of such alkoxy substitution ring closure may not proceed at all. Indeed even though the simple N-β-phenethyl-2-pyridone and N-β-phenethyl-2-quinolone had been made by Sugasawa and Sugimoto[1] no attempts were made to cyclise them to the corresponding quinolizines.*

The object of the study presented in this paper was to ascertain whether benzo- and dibenzoquinolizines could be synthesised by the Sugasawa procedure in the absence of activating alkoxy substituents. Quarternary salts were formed between β-phenethyl bromide and pyridine, α-picoline, quinoline and isoquinoline. These bromides have been reported previously.[3] Quarternary salts were also formed between β-(1-naphthyl) ethyl bromide and pyridine, quinoline, 4-methyl quinoline, 7-methyl quinoline and isoquinoline. These salts have not been reported before. They were crystalline solids, sparingly soluble in water and not at all hygroscopic unlike the quarternary salts with β-phenethyl bromide.

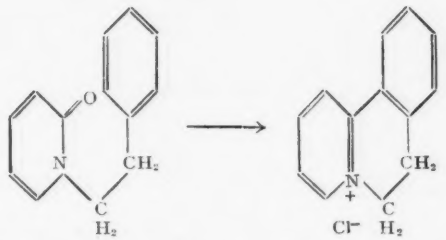
The oxidation of these quarternary salts was generally conducted at room temperature with alkaline potassium ferricyanide. N-β-phenethyl-α-picolinium bromide, N-β-phenethyl quinolinium bromide and N-β-(1-naphthyl) ethyl lepidinium bromide gave on oxidation only tarry oils under a variety of conditions. It was possible however to isolate the expected

* The material embodied in this paper formed part of a thesis submitted to the University of Madras in January 1953 for the Degree of Master of Science. While this paper was in preparation our attention has been drawn to a publication by Sugasawa *et al.* in the *J. Pharm. Soc. Jap.*, **72**, No. 10, p. 1275, in which the synthesis of three of the compounds prepared by us in the course of this study are reported.

oxidation product in crystalline condition by chromatographic fractionation of the tarry products, though in poor yields. The other quarternary salts were converted to the cyclic amides in excellent yield by oxidation with alkaline ferricyanide.

With the exception of N-β-phenethyl-6-methyl-2-pyridone, N-β-phenethyl-2-quinolone and N-β-(1-naphthyl) ethyl-4-methyl-2-quinolone, which were obtained in low yields, all the other cyclic amides were cyclised to the substituted quinolizinium salts by the action of phosphorous oxychloride and isolated as the quarternary iodides. The cyclisations have been found to proceed in excellent yields in all cases.

This remarkable ease of cyclisation is in striking contrast to the difficulty of cyclisation of acyl derivatives of β-phenethyl amine. The driving force in the present case appears to be the tendency of the heterocyclic part of the molecule to become fully aromatic.



The various quinolizinium iodides were reduced smoothly to the corresponding hydroquinolizines by reduction in alcohol medium in the presence of Adams' catalyst. The reduction products were purified by chromatography and characterised as hydrochlorides, picrates or picrolonates.

Experimental

β-phenethyl bromide was made by the method of Rupe.[4]

β-1-naphthyl ethyl bromide was made by the method of Haworth and Mavin.[5]

N-β-*phenethyl pyridinium bromide*

Pyridine (5 g.) and β-phenethyl bromide (10 g.) were refluxed in dry toluene (50 ml.) for three hours. A white crystalline solid separated on cooling. It was filtered and washed with absolute ether. On recrystallisation from absolute alcohol-ether mixture it was obtained in the form of lustrous needles melting at 125–126°; yield, 14·5 g. (Found: N, 5·5%; $C_{13}H_{14}NBr$ requires N, 5·3%).

Sugasawa and Sugimoto[1] report the melting point of this compound as 112°.

N-β-phenethyl pyridinium iodide

A solution of N-β-phenethyl pyridinium bromide (0·5 g.) in water (5 ml.) was treated with a saturated aqueous solution of potassium iodide (5 ml.). The precipitated iodide was crystallised from a mixture of absolute alcohol and ether and was obtained in the form of glistening needles melting at 166° (Found: N, 4·7%; $C_{13}H_{14}NI$ requires N, 4·5%).

N-β-phenethyl-2-pyridone

A solution of N-β-phenethyl pyridinium bromide (2·6 g.) in water (25 ml.) was added dropwise to a vigorously stirred aqueous solution of potassium ferricyanide (11·8 g.) and sodium hydroxide (3 g.) in the minimum amount of water. The solution was stirred for six hours at room temperature. The brown solid which separated was filtered, washed with water, dried and recrystallised from benzene, yielding colourless plates melting at 105°. The aqueous filtrate on extraction with benzene gave a small amount of the same pyridone. Yield, 1·3 g. (Found: C, 78·1%; H, 6·5%; N, 7·4%; $C_{13}H_{13}NO$ requires C, 78·4%; H, 6·5%; N, 7·0%).

3 : 4-dihydro-9 : 10-dehydro-1 : 2-benzoquinolizinium iodide

A solution of the above pyridone (1·5 g.) in absolute benzene (25 ml.) was refluxed with phosphorous oxychloride (12 ml.) for three hours. The reaction mixture was cooled and treated with a large excess of petroleum ether (b.p. 40–60°). After an hour, the solvent was decanted off from the black oil which had settled at the bottom. The oil was dissolved in dilute hydrochloric acid (0·2N, 25 ml.), warmed and filtered. The clear filtrate was treated with excess of a saturated aqueous solution of potassium iodide. The precipitated product was filtered, washed with water, dried and recrystallised from alcohol, when it was obtained as a fine yellow powdery material melting at 190°; yield, 1·9 g. (Found: C, 50·1%; H, 3·6%; N, 4·6%; $C_{13}H_{12}NI$ requires C, 50·5%; H, 3·9%; N, 4·5%).

3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzoquinolizine

A solution of the above benzoquinolizinium iodide (0·5 g.) in alcohol (100 ml.) was shaken with hydrogen at a pressure of 60 lb./sq. in. in the presence of Adams' catalyst (0·1 g.). When the absorption of hydrogen ceased, the solution was filtered to remove the catalyst and the filtrate distilled off to remove the solvent. The residue was dissolved in water and made alkaline. The liberated base was extracted with ether. On removal

of the solvent a reddish oil was obtained which could not be induced to solidify.

The picrate prepared in the usual way from this oil was recrystallised from alcohol when it was obtained in the form of yellow prisms melting at 123° (Found: C, 54·7%; H, 5·0%; N, 13·5%; $C_{19}H_{21}N_4O_7$ requires C, 54·7%; H, 5·0%; N, 13·4%).

The picrolonate prepared by mixing alcoholic solutions of the oil and picrolonic acid was crystallised from alcohol when it was obtained in the form of yellow needles melting at 205° (Found: C, 60·8%; H, 5·6%; N, 15·6%; $C_{23}H_{26}N_5O_5$ requires C, 61·1%; H, 5·8%; N, 15·5%).

The following compounds were prepared by methods analogous to those described above.

3:4:5:6-*tetrahydro*-1:2:7:8-*dibenzoquinolizine*

N-β-*phenethyl isoquinolinium bromide*.—It was crystallised from a mixture of absolute alcohol and ether and was obtained in the form of shining needles melting at 73° (Found: N, 4·8%; $C_{17}H_{16}NBr$ requires N, 4·5%). *N*-β-*phenethyl isoquinolinium iodide* was crystallised from alcohol when it was obtained in the form of colourless needles melting at 177° (Found: N, 4·0%; $C_{17}H_{16}NI$ requires N, 3·9%). *N*-β-*phenethyl isoquinolone*-1 was obtained by oxidation of the quarternary bromide with alkaline ferricyanide. Crystallisation from benzene gave pale yellow plates melting at 102°. 3 g. of the quarternary bromide yielded 2·1 g. of the isoquinolone (Found: C, 82·2%; H, 6·2%; N, 5·9%; $C_{17}H_{15}NO$ requires C, 81·9%; H, 6·0%; N, 5·6%). 3:4-*dihydro*-9:10-*dehydro*-1:2:7:8-*dibenzoquinolizinium iodide*, obtained by the cyclisation of the above isoquinolone was recrystallised from water. It separated as yellow needles melting at 120°. After drying at 100° for three hours *in vacuo* it melted at 155°. 2 g. of the isoquinolone gave 2·4 g. of the quinolizinium iodide (Found: C, 56·6%; H, 3·8%; N, 4·1%; $C_{17}H_{14}NI$ requires C, 56·8%; H, 3·9%; N, 3·9%).

3:4:5:6-*tetrahydro*-1:2:7:8-*dibenzoquinolizine* was obtained by catalytic reduction of the above iodide and was obtained in the form of an oil. When the oil was treated with hydrochloric acid the hydrochloride was formed which on recrystallisation from dilute alcohol was obtained as a fine powder, melting at 207° (Found: C, 74·7%; H, 6·9%; N, 5·3%; $C_{17}H_{19}NCl$ requires C, 74·9%; H, 7·0%; N, 5·1%). The picrolonate of the above base was crystallised from alcohol when it was obtained as yellow needles melting at 169° (Found: C, 64·5%; H, 5·1%; N, 14·2%; $C_{27}H_{26}N_5O_5$ requires C, 64·8%; H, 5·2%; N, 14·0%).

N-β-phenethyl-α-picolinium bromide was obtained as colourless needles by crystallisation from alcohol and was found to melt at 198° (Found: N, 5·2%; $C_{14}H_{16}NBr$ requires N, 5·0%). *N-β-phenethyl-6-methyl-2-pyridone* obtained by alkaline ferricyanide oxidation of the above quarternary salt and subsequent chromatographic fractionation of the oily material was a colourless crystalline solid. On recrystallisation from petroleum ether it was obtained in the form of colourless plates melting at 108° (Found: C, 78·6%; H, 6·7%; N, 6·9%; $C_{14}H_{15}NO$ requires C, 78·9%; H, 7·0%; N, 6·6%).

N-β-phenethyl-2-quinolone.—The quarternary bromide formed between β-phenethyl bromide and quinoline could not be obtained in the form of a solid and the oily material as such was oxidised with alkaline ferricyanide. The product again was an oil which on chromatographic fractionation over alumina and recrystallisation from petroleum ether, was obtained in the form of colourless plates melting at 98° (Found: C, 81·8%; H, 5·9% N, 6·0%; $C_{17}H_{15}NO$ requires C, 81·9%; H, 6·0%; N, 5·6%).

N-β-(1-naphthyl) ethyl pyridinium bromide was obtained as colourless needles by crystallisation from alcohol. It melted at 110° (Found: N, 4·6%; $C_{17}H_{16}NBr$ requires N, 4·5%). *N-β-(1-naphthyl) ethyl pyridinium iodide* was crystallised from alcohol when it separated in the form of colourless needles melting at 120° (Found: N, 4·0%; $C_{17}H_{16}NI$ requires N, 3·9%). *N-β-(1-naphthyl) ethyl-2-pyridone.* It was obtained as colourless plates by recrystallisation from alcohol. It melted at 72° (Found: C, 81·7%; H, 6·0%; N, 5·7%; $C_{17}H_{15}NO$ requires C, 81·9%; H, 6·0%; N, 5·6%). *3:4-dihydro-9:10-dehydro-1:2:1′:2′-naphthoquinolizinium iodide*, obtained by the cyclization of the above pyridone, was recrystallised from aqueous alcohol when it separated as a fine white powder melting at 177° (Found: C, 49·2%; H, 4·4%; N, 3·7%; $C_{17}H_{14}NI·3H_2O$ requires C, 49·4%; H, 4·8%; N, 3·4%). *3:4:5:6:7:8-hexahydro-1:2:1′:2′-naphthoquinolizine* was obtained by the catalytic reduction of the above iodide. It was an oil, treatment of which with hydrochloric acid gave the hydrochloride. The latter was recrystallised from water when it was obtained in the form of a fine white powder melting at 218° (Found: C, 78·1%; H, 6·3%; N, 4·5%; $C_{21}H_{21}NCl$ requires C, 78·1%; H, 6·5%; N, 4·3%). The hexahydro base gave a crystalline picrate which on recrystallisation from alcohol was obtained as yellow needles, melting at 157° (Found: C, 62·5%; H, 4·3%; N, 11·0%; $C_{27}H_{23}N_4O_7$ requires C, 62·9%; H, 4·5%; N, 10·9%).

N-β-(1-naphthyl) ethyl isoquinolinium bromide was obtained as pale brown needles by crystallisation from absolute alcohol-ether mixture. It

melted at 158° (Found: N, 3·9%; $C_{21}H_{18}NBr$ requires N, 3·8%). *N*-β-(1-*naphthyl*) *ethyl isoquinolinium iodide* was obtained as yellow powder on recrystallisation from alcohol. It melted at 190° (Found: N, 3·5%; $C_{21}H_{18}NI$ requires N, 3·4%).

N-β-(1-*naphthyl*) *ethyl*-1-*isoquinolone* was prepared by oxidation of the bromide with alkaline ferricyanide and was obtained as colourless plates by recrystallisation from alcohol. It melted at 97°. 7 g. of the bromide gave 4·3 g. of the isoquinolone (Found: C, 83·7%; H, 5·5%; N, 4·3%; $C_{21}H_{17}NO$ requires C, 84·2%; H, 5·6%; N, 4·6%). 3:4-*dihydro*-9:10-*dehydro*-1:2:1′:2′-*naphtho*-7:8-*benzoquinolizinium iodide* was made by the cyclisation of the above isoquinolone. 2·6 g. of the iodide was obtained from 2 g. of the former. On recrystallisation from alcohol it separated as a yellow powder melting at 192° (Found: C, 61·4%; H, 3·8%; N, 3·7%; $C_{21}H_{16}NI$ requires C, 61·6%; H, 3·9%; N, 3·4%).

3:4:5:6-*tetrahydro*-1:2:1′:2′-*naphtho*-7:8-*benzoquinolizine* was obtained by the catalytic reduction of the above base and subsequent chromatographic fractionation of the oil got. It was recrystallised from alcohol when it separated as colourless white plates melting at 98° (Found: C, 88·5%; H, 7·2%; N, 5·1%; $C_{21}H_{20}N$ requires C, 88·1%; H, 7·0%; N, 4·9%). The picrate of the above base on recrystallisation from alcohol was obtained as a yellow powder melting at 209° (Found: C, 63·2%; H, 4·7%; N, 11·1%; $C_{27}H_{23}N_4O_7$ requires C, 62·9%; H, 4·5%; N, 10·9%). The picrolonate of the base was crystallised from alcohol and was obtained as a yellow powdery solid melting at 190° (Found: C, 67·4%; H, 5·3%; N, 12·9%; $C_{31}H_{28}N_5O_5$ requires C, 67·6%; H, 5·1%; N, 12·7%).

N-β-(1-*naphthyl*) *ethyl quinolinium bromide* was obtained as a colourless powdery solid on recrystallisation from water. It melted at 172° (Found: N, 3·7%; $C_{21}H_{18}NBr$ requires N, 3·8%). *N*-β-(1-*naphthyl*) *ethyl quinolinium iodide* prepared from the above bromide was recrystallised from alcohol when it separated in the form of fine needles, melting at 204° (Found: N, 3·5%; $C_{21}H_{18}NI$ requires N, 3·4%). *N*-β-(1-*naphthyl*) *ethyl*-2-*quinolone* obtained by the oxidation of the bromide was crystallised from dilute alcohol when it separated in the form of pale brown flakes melting at 172° (Found: C, 83·9%; H, 5·6%; N, 4·3%; $C_{21}H_{17}NO$ requires C, 84·3%; H, 5·7%; N, 4·7%).

3:4-*dihydro*-9:10-*dehydro*-1:2:1′:2′-*naphtho*-5:6-*benzoquinolizinium iodide*, the product obtained on cyclisation of the above quinolone was crystallised from alcohol when it was got as a yellow powdery solid melting at 193° (Found: C, 61·4%; H, 3·8%; N, 3·6%; $C_{21}H_{16}NI$ requires C, 61·6%; H, 3·9%; N, 3·4%).

3:4:7:8-*tetrahydro*-1:2:1′:2′-*naphtho*-5:6-*benzoquinolizine* was obtained by catalytic reduction of the above base and purified by recrystallisation from alcohol after passing through a column of alumina. It was obtained in the form of colourless flakes melting at 117° (Found: C, 88·4%; H, 7·2%; N 5·0%; $C_{21}H_{20}N$ requires C, 88·1%; H, 7·0%; N, 4·9%). The picrate of the base was crystallised from alcohol when it separated as yellow needles melting at 77° (Found: C, 63·1%; H, 4·6%; N, 10·9%; $C_{27}H_{23}N_4O_7$ requires C, 62·9%; H, 4·5%; N, 10·9%).

N-β-(1-*naphthyl*) *ethyl*-7-*methyl quinolinium bromide*, prepared in the usual way was crystallised from alcohol-ether and was obtained in the form of colourless plates melting at 194° (Found: N, 3·9%; $C_{22}H_{20}NBr$ requires N, 3·7%). N-β-(1-*naphthyl*) *ethyl*-7-*methyl quinolinium iodide* was crystallised from alcohol and was obtained as a pale yellow powder melting at 225° (Found: N, 3·5%; $C_{22}H_{20}NI$ requires N, 3·3%). *N*-β-(1-*naphthyl*) *ethyl*-7-*methyl*-2-*quinolone*, obtained by the oxidation of the bromide was recrystallised from petroleum ether when it separated in the form of pale brown flakes melting at 136°(Found: C, 84·2%; H, 6·3%; N, 4·8%; $C_{22}H_{19}NO$ requires C, 84·4%; H, 6·1%; N, 4·5%). 3:4-*dihydro*-9:10-*dehydro*-1:2:1′:2′-*naphtho*-5:6:1″:2″-*benzo*-4″-*methyl benzoquinolizinium iodide* obtained from the above quinolone was crystallised from alcohol when it separated as pale yellow powder melting at 181° (Found: C, 62·7%; H, 4·6%; N, 3·4%; $C_{22}H_{18}NI$ requires C, 62·4%; H, 4·3%; N, 3·3%).

3:4:7:8-*tetrahydro*-1:2:1′:2′-*naphtho*-5:6:1″:2″-*benzo*-4″-*methyl benzoquinolizine* was obtained by the reduction of the foregoing iodide and on recrystallisation from alcohol after chromatographic purification it separated in the form of colourless needles melting at 131° (Found: C, 88·3%; H, 7·5%; N, 4·9%; $C_{22}H_{22}N$ requires C, 88·0%; H, 7·3%; N, 4·7%). The picrate of the above base prepared in the usual way was crystallised from alcohol when it was obtained as yellow needles melting at 145° (Found: C, 63·8%; H, 4·5%; N, 10·7%; $C_{28}H_{25}N_4O_7$ requires C, 63·5%; H, 4·7%; N, 10·5%).

N-β-(1-*naphthyl*) *ethyl*-4-*methyl quinolinium bromide* was crystallised from absolute alcohol-ether when it separated in the form of shining plates melting at 196° (Found: N, 3·9%; $C_{22}H_{20}NBr$ requires N, 3·7%).

N-β-(1-*naphthyl*) *ethyl*-4-*methyl*-2-*quinolone* obtained by the oxidation of the above bromide was an oil which on chromatographic fractionation gave a crystalline solid. The latter on recrystallisation from petroleum ether was obtained as a colourless powder melting at 98° (Found: C, 84·1%; H, 6·1%; N, 4·7%; $C_{22}H_{19}NO$ requires C, 84·3%; H, 6·1%; N, 4·5%).

Summary

The scope of the Sugasawa method for the synthesis of quinolizinium derivatives has been investigated. Several benzo, naphtho and naphthobenzo quinolizinium compounds have been synthesised in excellent yields, although the ring on which cyclisation was effected did not carry any activating substituents.

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COLOURING MATTER OF THE FLOWER PETALS OF *BAUHINIA TOMENTOSA* LINN.

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Bauhinia tomentosa Linn. is a short shrubby garden plant (family Leguminosæ) occurring in central and south India and bears pale sulphur yellow flowers. The flower pigments of the Bauhinia species do not seem to have been examined so far. From the leaves of *Bauhinia reticulata*, however, was isolated quercitrin in 0·5% yield by Rabate.[1]

In the present investigation the sun-dry Bauhinia flowers were extracted with alcohol. On concentration, the main colouring matter was obtained. The ethereal extract of the mother liquor yielded quercetin. No crystalline substance could be isolated from the mother liquor by means of the lead salt method.

The main colouring matter was a quercetin glycoside and on hydrolysis with acid gave rise to quercetin and an equimolecular mixture of *d*-glucose and *l*-rhamnose. From its properties and reactions it was considered to be rutin. This was confirmed by complete methylation and subsequent hydrolysis whereby was obtained 3-hydroxy-5 : 7 : 3′ : 4′-tetramethoxy flavone.

The yield of rutin from the Bauhinia flowers is 4·6% and compares favourably with that of the American buckwheat[2] (6%). In view of the reported beneficial action of rutin on capillary fragility in man,[3] the flowers of *Bauhinia tomentosa* may be a useful source of rutin.

Experimental

The flowers used in this investigation were collected from the local gardens in Waltair during the period of July to September. The sun-dried flowers (225 g.) were refluxed with alcohol (1,000 c.c.) for six hours and decanted hot. This was repeated three times. The combined extracts (1,800 c.c.) deposited some wax on cooling which was filtered and the filtrate distilled to recover most of the solvent. The residual liquid (120 c.c.) deposited a large quantity of an yellow solid (marked A) on leaving for a week along with excess of ether. It was filtered and washed with ether; yield 9·5 g. The ether layer was separated and marked B.

The alcoholic mother liquor was evaporated to remove all alcohol and the residue stirred up with boiling water (200 c.c.) and the solution filtered from waxy and resinous matter. It was concentrated to half its volume, treated with an equal volume of ether and left in the ice-chest for about a fortnight. About 1 g. more of A was obtained.

The ether solution B : Quercetin.—When evaporated, it left behind a pale brown crystalline solid (0·5 g.) which after two crystallisations from alcohol gave yellow needles decomposing at 313–15°, not depressed by admixture with an authentic sample of quercetin. The acetate crystallised from alcohol as colourless needles melting at 193–5°, unchanged when mixed with penta acetyl quercetin.

Solid product A: Rutin.—When crystallised first from alcohol and then from aqueous pyridine it came out as pale yellow short needles melting at 188–90°. It did not depress the melting point of an authentic sample of rutin (Found in the sample dried at 100° *in vacuo*: C, 53·0; H, 5·0. $C_{27}H_{30}O_{16}$ requires C, 53·1; and H, 5·0%). In 85% alcoholic solution, it had $[\alpha]_D^{28°}$ + 38·8° (Plouvier[4] reported $[\alpha]_D$, +39° for rutin in pyridine solution).

An alcoholic solution of the glycoside yielded an yellow precipitate with neutral lead acetate, a deep green colour with ferric chloride and a deep pink colour with magnesium and hydrochloric acid. A solution in concentrated sulphuric acid exhibited a greenish fluorescence.

Hydrolysis.—The pure glycoside (1 g.) was refluxed with 9% sulphuric acid for two hours. The aglycone, which separated even during the course of refluxing, was filtered and crystallised from alcohol; bright yellow needles m.p. 313–15° (decomp.), undepressed by admixture with an authentic sample of quercetin; yield 0·55 g. It answered all the colour reactions for quercetin. Methylation of the aglycone with dimethyl sulphate and potassium carbonate in anhydrous acetone solution yielded 0-pentamethyl quercetin, m.p. 150–51° identical with an authentic sample.

The pale yellow acid filtrate from quercetin was extracted twice with ether and then neutralised with barium carbonate. It was evaporated at 30° *in vacuo* and the sugar residue extracted with absolute alcohol. The alcoholic extract was evaporated under reduced pressure and the sugar converted into osazone directly in the usual manner. When crystallised from aqueous alcohol it melted at 195–200°. Under the microscope, it was not homogeneous but the characteristic sheave-like clusters suggested the presence of phenyl glucosazone. Further the neutral sugar syrup answered the methyl furfural test for *l*-rhamnose. The acid hydrolysate (from 36·6 mg.

made up to 25 c.c.) gave a specific rotation of + 30·03°. Plouvier[4] gave a value of + 29° for the hydrolysate from rutin.

Methylation of the glycoside and hydrolysis : 0-*Tetramethyl Quercetin.*—

A suspension of finely powdered glycoside (2 g.) in dry acetone (150 c.c.) was refluxed with dimethyl sulphate (10 c.c. added in two lots) and potassium carbonate (20 g.) for 30 hours. The mixture was filtered, the pale brown acetone filtrate concentrated and the oily brown residue directly hydrolysed by refluxing with 7% sulphuric acid for two hours. On cooling, the solution deposited pale yellow needles melting at 197–98°, which was not depressed by an authentic sample of 3-hydroxy-5 : 7 : 3′ : 4′-tetramethoxy flavone.[5] Yield 0·8 g. (Found : C, 63·9; H, 5·3. $C_{19}H_{18}O_7$ requires C, 63·7; and H, 5·0%). It was easily soluble in aqueous alkali to give an yellow solution and exhibited dark brown colour with ferric chloride in alcoholic solution.

The above hydroxy flavone (1 g.) was refluxed for six hours with diethyl sulphate (1 c.c.) and anhydrous potassium carbonate (4 g.) in acetone solution. The ethyl methyl ether crystallised from alcohol as colourless narrow rectangular needles melting at 154–55°, undepressed by a synthetic sample of 3-ethoxy-5 : 7 : 3′ : 4′-tetramethoxy flavone.[5] (Found : C, 65·2; H, 5·8. $C_{21}H_{22}O_7$ requires C, 65·3; and H, 5·7%).

We are indebted to Prof. T. R. Seshadri, Delhi University, for his interest in this investigation and to the Curator, Royal Botanic Gardens, Sibpur, for the identification of the plant.

SUMMARY

Rutin was isolated in an yield of 4·6% from the flowers of *Bauhinia tomentosa* Linn. They contained quercetin also in small quantities.

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THE ROTATORY DISPERSION OF BENZIL

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1. Introduction

Benzil ($C_6H_5.CO.CO.C_6H_5$) is a yellow solid which crystallises in the form of hexagonal prisms belonging to the space-groups D_3^4 and the enantiomorphous D_3^6. The structure of benzil has not been fully determined; but it is known that the unit cell contains three skew molecules disposed spirally about the principal axis and in such a way that the benzene rings are more nearly parallel than perpendicular to the axis. The substance is optically active in the crystalline state. This has been measured by Des Cloizeaux (1870), who finds the rotatory power for λ 5893 Å to be slightly greater than that of quartz.

The refractive dispersion and birefringence of benzil have been studied in detail by E. E. Jelley (1941) and W. M. D. Bryant (1943). The optical behaviour of this crystal exhibits certain interesting features. For λ 5893 Å, the crystal is uniaxial and *positive*, the birefringence being slightly greater than that of quartz. As we proceed towards the violet, the birefringence progressively decreases, till at λ 4205 Å the crystal is optically *isotropic*. Beyond that wavelength, the birefringence reverses sign, the crystal then becoming uniaxial and *negative*.

These optical properties are evidently related to the absorption spectrum of the substance. The ultraviolet absorption spectrum of benzil dissolved in organic solvents has been studied by several workers. It will suffice here to quote the data given in the International Critical Tables (1930). The benzil solution has a comparatively weak absorption which extends from 4500 Å onwards into the shorter wavelength side of the spectrum, with a maximum lying at about 3900 Å. This absorption is the cause of the characteristic yellow colour of the substance. There is a much more intense absorption at 2500 Å and another still more intense farther out in the extreme ultraviolet.

The present investigation was taken up with a view to determine the rotatory dispersion of benzil over a wide range of wavelengths and to correlate it with its absorption spectrum. Measurements have been possible from

about 9000 Å in the infrared upto about 3600 Å in the ultraviolet right through an absorption band. Some interesting results have emerged which will be described in the course of the paper. In some earlier papers published in these *Proceedings* (Chandrasekhar, 1952, 1953), we have already examined the rotatory dispersion of quartz, sodium chlorate and cinnabar. We shall now proceed to consider the case of benzil.

2. PREPARATION OF THE CRYSTALS

The commercially available chemical was first purified by repeated crystallisation by evaporation of a solution of the substance in alcohol or ether. The crystals thus obtained are generally in the form of needles and hence not very suitable for the present study. Since the melting point of benzil is only 95° C., bigger crystals could be grown from the melt without much difficulty. The purified substance was taken in a glass tube tapered at the bottom and melted in an electric furnace. The furnace was so constructed that a steady current through its heater coil established a temperature gradient down its length, the lower portion being a few degrees cooler. The tube was slowly lowered at the rate of a few millimetres per hour by means of a clockwork arrangement. The tapered bottom facilitates the crystallisation to start from a point. Crystals of about 0·5 to 1 cm. length were obtained after a few trials. The optic axes of these crystals, which were ascertained by observation through a pair of polaroids, generally coincided with the direction of the temperature gradient. After several crystallisations, a few clear transparent specimens were selected for the present study. Amongst these, both right and left rotating crystals were present.

The crystals are extremely soft and brittle so that great care had to be exercised in cutting and polishing them. They were ground by means of very fine carborundum and polished with rouge spread on wet chamois leather. When extremely thin specimens less than 0·03 mm. thick had to be prepared, the crystal, properly cut, was first stuck on by means of a very thin layer of canada balsam (whose rotatory power is negligible) to a glass plate to prevent its fracture and then slowly rubbed down to the required thickness. Very fine carborundum and in the later stages rouge itself was found to be suitable for the grinding.

3. THE ULTRAVIOLET TRANSMISSION SPECTRUM

The earlier investigations on the ultraviolet absorption spectrum of benzil appear to be restricted to solutions of the substance in organic solvents. It was therefore thought worthwhile to make at least a qualitative study of the transmission spectrum of crystalline benzil. A tungsten filament lamp

served as a convenient continuous source of light. Transmission photographs were taken with a Hilger medium quartz spectrograph for varying thicknesses of the crystal ranging from about 1 cm. to about 0·02 mm. These have been reproduced in Fig. 1, Plate XXI. For each thickness of the crystal three exposures have been given, increasing from a few seconds to 10 minutes. Proceeding upwards, the successive groups of three exposures each were taken with specimens of thicknesses roughly 1 cm., 1 mm., 0·1 mm., 0·05 mm. and 0·02 mm. respectively. The exposure just below the wavelength scale is that of the lamp itself. It will be noticed that as the thickness is reduced,the limit of transmission shifts in a step-like fashion. One can also see the notable diminution in the intensity beyond 4000 Å even in the thinner specimens. This marks the presence of an absorption band in that region of the spectrum which extends upto 4500 Å for thicker crystals. But, even with the thinnest crystals, there is an almost sharp cut off beyond 3400 Å. This is evidently the beginning of the very intense absorption lying farther out in the ultraviolet.

Fig. 2, Plate XXI reproduces photographs taken with a tungsten lamp and a mercury arc respectively, which demonstrate the pleochroism exhibited by benzil. A crystal about 0·05 mm. thick, cut parallel to the optic axis was used for this purpose. In both Figs. 2 (*a*) and 2 (*b*), the upper exposure is the transmission for light polarised with the electric vector perpendicular to the optic axis, *i.e.*, for the ordinary ray, while the lower one is the transmission for the electric vector parallel to the optic axis or the extraordinary ray. An inspection of Fig. 2 (*a*) will make it clear that in the region of 4000 Å there is greater absorption for the ordinary ray than for the extraordinary ray, whereas the reverse is the case at about 3600 Å. This is even more obvious in Fig. 2 (*b*) where the transmissions for λ 4046 Å and λ 3665 Å are clearly oppositely polarised. Broadly speaking, we may state that the effective absorption maximum for the ordinary ray is at a slightly longer wavelength than that for the extraordinary ray. As we shall see later, this fact will be useful in explaining the refractive dispersion and birefringence of benzil over the range of wavelengths for which data is available.

Ganguly and Choudhury (1953) have studied the polarisation of the fluorescence of crystalline benzil. They find that, irrespective of whether the incident light is polarised or not, the fluorescent light is partially polarised, the vibrations $\perp$ to the optic axis being stronger than the $\parallel$ vibrations. It is interesting to find that a somewhat similar result has been obtained in our absorption studies, the $\perp$component being more absorbed than the $\parallel$ component. These results are evidently related to the molecular orienta-

tions in the crystal, but as the structure of the molecule itself has not been definitely established it would be premature at this stage to discuss this aspect of the problem.

The transmission spectrum of benzil dissolved in benzene was also photographed, though this has not been reproduced here. Upto the wavelength studied (3400 Å), both the crystal and the solution exhibit very similar features, except that the positions of the absorptions of the solution are slightly shifted towards longer wavelengths as compared to those of the crystal. A cursory examination of the transmission of light by benzil vapour revealed that its absorption spectrum is not very much different from that of the crystal or the solution.

4. MEASUREMENT OF THE ROTATORY DISPERSION

The polarimeter consisted of two nicols, one of which was mounted on a divided circle and served as the analyser. By a suitable system of lenses, light from a mercury arc was made to pass through the polarimeter and the crystal and focus on the widened slit of a spectrograph. Photographs of the spectrum were taken with different settings of the analyser, the time of exposure for the successive photographs being made exactly the same varying from a few minutes to half an hour depending on the region of the spectrum which was being studied. By finding out the exposures of equal intensity on either side of the minimum, the position of extinction could be determined for each wavelength to within a fraction of a degree.

For the range between λ 5893 Å and λ 4916 Å, a specimen of thickness 7·95 mm. (measured by the micrometer caliper) was used. The thickness had to be reduced to about 1 mm. before λ 4358 Å (Hg) was feebly transmitted and measurement was then possible for that wavelength. The next step was to try and penetrate the absorption band and to pursue the measurements upto at least 3600 Å°. For this a crystal cut perpendicular to the optic axis of thickness less than 0·03 mm. had to be used. The specimen was prepared in the manner already described. It was thinned down till the λ 4046 Å line was faintly visible after passage through it. In these circumstances, it was found that the transmission extended upto about 3600 Å, so that the measurement of the rotatory power could be extended upto that wavelength.

Similarly, measurements were carried out into the infra-red region of the spectrum upto about 9000 Å. The mercury arc was a good source of light but specially sensitized photographic plates (Kodak IRER) were necessary.

The thickness of the largest crystal was measured by means of a micrometer caliper and those of the other two were estimated in terms of this thickness by a comparison of the values of the rotations for certain common wavelengths. The accuracy of measurement with the first two specimens is quite high, as the value of the total rotations for these thicknesses is large. But with the thinnest specimen the total rotation is hardly a few degrees and this could be determined only to within about 0·1°, so that the accuracy of measurement is considerably less. The values of the total rotations obtained with the three specimens for the different wavelengths together with the mean estimated value of the rotatory power are given in Table I. Throughout, the wavelength (λ) is expressed in microns (μ) and the rotatory power in degrees per millimetre.

TABLE I

λ (in μ)	Total Rotation measured in degrees			Mean Value of Rotatory Power
	Specimen I Thickness measured 7·95 mm.	Specimen II Thickness estimated 1·08 mm.	Specimen III Thickness estimated 0·0281 mm.	
·3590			4·2	149
·3655			4·08	145
·3704			3·70	132
·3785			3·20	114
·3906			2·70	96
·3980			2·20	78
·4046			1·50	53
·4078			1·35	48
·4358		48·4	1·25	44·8
·4916	330·63	44·9	1·14	41·6
·5461	245·38	33·9	0·89	31·4
·5780	212·13	28·9	0·78	26·7
·5893	202·13	27·15		25·3
·6234		23·4		21·7
·6908		18·4		17·0
·7082		16·4		15·2
·7729		13·4		12·4
·8180		12·4		11·5
·8756		10·4		9·6

The rotatory power for λ 5893 Å as determined by Des Cloizeaux is $25° \pm 0·3°$. This value is in good agreement with that obtained in the present work.

It has been shown earlier by the present author that the rotatory dispersion of quartz and cinnabar are represented much better by a formula of the type

$$\rho = \frac{k\lambda^2}{(\lambda^2-\lambda_0^2)^2} \tag{1}$$

than by a formula of the Drude type. Benzil is in many respects very similar to the two crystals mentioned above. For instance, it crystallises in the same space-group to which quartz and cinnabar belong and also, like the latter, its optical activity, is present only in the crystalline state. Hence we may expect that the rotatory dispersion of benzil to be represented well by a similar formula. The following formula fits the experimental data fairly well:

$$\rho = \frac{6\cdot27\ \lambda^2}{[\lambda^2 - (0\cdot24)^2]^2} \tag{2}$$

It has been found necessary to assume a characteristic absorption wavelength at 2400 Å in order to fit the data accurately. The absorption spectrum of crystalline benzil has not been studied in the ultraviolet, but one can see that this assumed wavelength roughly corresponds to the actual absorption observed at about 2500 Å in the benzil solution. The small shift of about 100 Å may be expected to be a genuine one from what we have seen earlier regarding the differences in the transmission spectrum of the solution and the crystal. The absorption band at 3900 Å has been neglected altogether as it is a comparatively weak one and as we shall see later contributes only a little to the rotatory power. Further, an exact knowledge of the intensity and shape of the absorption is necessary before we can attempt at fitting a formula which is valid right through the band. There has been no necessity to include a term involving the extreme ultraviolet absorption in this formula, whereas this term contributes considerably to refraction. The values calculated from the formula have been drawn as a continuous curve in Fig. 1, while the experimental data have been plotted as points. The crystal exhibits anomalous rotatory dispersion in the neighbourhood of the absorption band. However, except in the immediate vicinity of the band, the experimental points fall on the theoretical curve. The shaded portion in the graph represents the actual contribution of the absorption band to the rotatory power, and this is not large. We are, therefore, not unjustified in leaving it out in our formula. It is interesting to find that the same type of formula that holds good for quartz and cinnabar also represents the data for benzil fairly well.

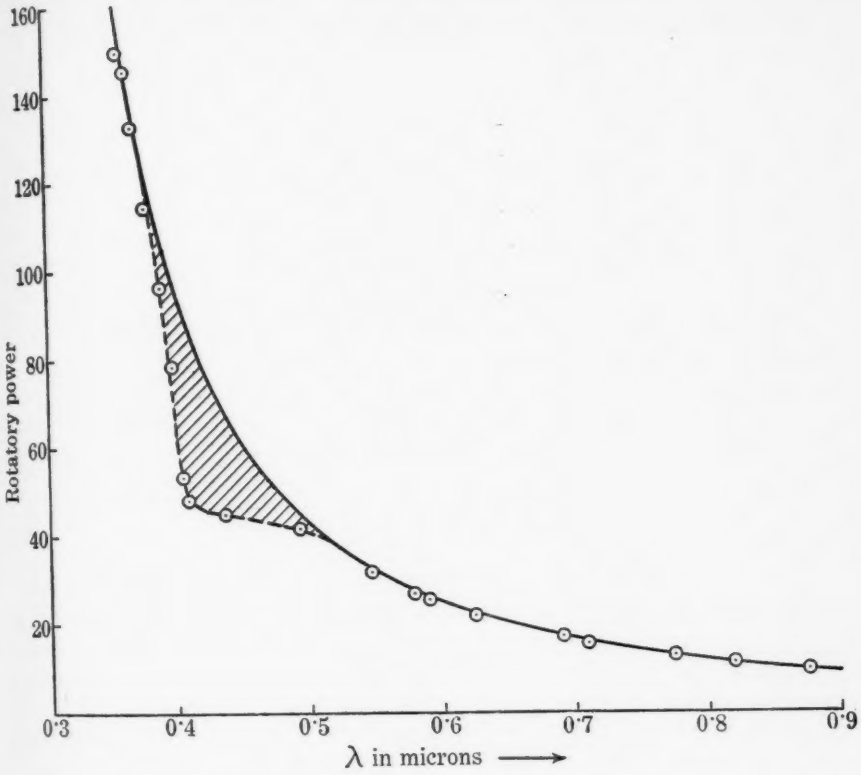


FIG. 1. The Rotatory Dispersion of Benzil.

5. THE THERMAL VARIATION OF THE ROTATORY POWER

An attempt was then made to see if the rotatory power shows any marked changes when the temperature of the crystal is altered. A specimen about 5 mm. thick was used for this experiment. The crystal was mounted inside a solenoid suitably constructed for the purpose, so that it could be heated electrically. The temperature of the crystal was measured by means of a copper-constantan thermocouple. The rotatory power was determined both at room temperature (28° C.) and at 68° C. The rotatory power is found to decrease slightly with rise of temperature. The values of the rate of variation of the rotatory power with temperature, $d\rho/dt$, are given in Table II for three wavelengths. High accuracy cannot however be claimed for these values as the changes in rotation are rather small.

TABLE II

λ	$-d\rho/dt \times 10^2$ (28° to 68° C.)
·4916	2·5
·5461	2·0
·5780	1·5

In some earlier papers, the present author has shown that the thermal variation of the rotatory power of quartz and cinnabar can be satisfactorily explained by assuming that the characteristic frequencies shift with temperature. We shall not make a similar calculation in the case of benzil, as a detailed knowledge of the contribution of the negative term at 3900 Å is necessary before we can proceed to do so.

6. THE REFRACTIVE DISPERSION OF BENZIL

The following formulæ of the Sellmeier-Drude type have been found to fit the refractive dispersion of benzil over the whole range of available data:

$$\epsilon^2 - 1 = 1{\cdot}35 + \frac{0{\cdot}37\,\lambda^2}{\lambda^2 - (0{\cdot}24)^2} + \frac{0{\cdot}0138\,\lambda^2}{\lambda^2 - (0{\cdot}395)^2} \tag{3}$$

$$\omega^2 - 1 = 1{\cdot}08 + \frac{0{\cdot}535\,\lambda^2}{\lambda^2 - (0{\cdot}24)^2} + \frac{0{\cdot}015\,\lambda^2}{\lambda^2 - (0{\cdot}398)^2} \tag{4}$$

The characteristic absorption wavelength at 2400 Å which occurs in the rotatory dispersion formula (2) also appears in these formulæ. In addition, the extraordinary index has a characteristic dispersion wavelength at 3950 Å while the ordinary index has one at 3980 Å. This is based on the observations made earlier regarding the pleochroism of crystalline benzil in the region of 4000 Å. The contribution of the extreme ultraviolet term has been replaced by a constant in each formula. The calculated values are given in comparison with Bryant's experimental data in Table III.

The agreement between the experimental and the calculated values is quite good. The interesting way in which the birefringence of benzil varies as we proceed from one end of the visible spectrum to the other becomes immediately explicable in terms of these dispersion formulæ.

TABLE III

λ	ϵ (expt.)	ϵ (calc.)	ω (expt.)	ω (calc.)	$\epsilon-\omega$ (expt.)	$\epsilon-\omega$ (calc.)
·4205	1·737	1·737	1·737	1·737	0·000	0·000
·4358	1·720	1·720	1·716	1·714	0·004	0·006
·4380	1·718	1·718	1·712	1·712	0·006	0·006
·4620	1·705	1·705	1·694	1·694	0·011	0·011
·4860	1·695	1·697	1·682	1·683	0·013	0·014
·5461	1·684	1·684	1·667	1·666	0·017	0·018
·5780	1·680	1·680	1·660	1·660	0·020	0·020
·5893	1·679	1·679	1·658	1·658	0·021	0·021
·6560	1·672	1·673	1·648	1·648	0·024	0·023

7. DISCUSSION

The structure of the benzil molecule is not definitely known. Caldwell and Le Fevre (1939), from a measurement of the dipole moment of benzil dissolved in various organic solvents, suggest that the molecule has a skew configuration in which the two $C_6H_5-\overset{|}{C}=O$ groups lie in planes which are nearly mutually perpendicular. In such a case, the molecule can obviously exist in either a right-handed or a left-handed form. The optical activity of benzil should consequently be of molecular origin, as is the case, for instance, with the sugars, the tartrates, etc. But remarkably enough, the rotatory power of this substance exists only in the crystalline state. The reason for this perhaps lies in the fact that in the state of solution, an interchange or equilibrium between the *d* and the *l*-forms of the molecule exists—a possibility which cannot be precluded if the potential barrier between these two enantiomorphous forms is not large. Or it may be that there is a free rotation of the two halves of the molecule about the central C—C bond. In fact, the measured value of the dipole moment of benzil in solution agrees closely with the value computed assuming a free rotation. But Caldwell and Le Fevre are inclined to dismiss such a possibility. In the crystal, on the other hand, the molecule would assume a relatively fixed configura-

tion, as is evident from the fact that the rotatory power does not exhibit any catastrophic change when the crystal is heated.

A large amount of experimental data concerning various properties of crystalline benzil is available. However, these data still await interpretation on account of the fact that the structure of the crystal is not known. For instance, the magnetic anisotropy of benzil is quite large and comparable in magnitude with that of naphthalene, biphenyl, etc. (Krishnan, Guha and Banerjee, 1933). The optical anisotropy, on the contrary, is quite feeble. In fact, the crystal is optically isotropic in the violet region of the spectrum. An explanation for this in terms of the crystal structure and the anisotropies of the individual molecules would be of the highest interest. But, only a preliminary analysis of the crystal structure has been made so far and that is by Knaggs and Lonsdale (1939), who have come to the conclusion that the molecule must be of a skew type. Mann and Thompson (1951) have examined the polarisation of the infra-red absorption of benzil with a view to get some information about the structure, but have not arrived at anything significant from their observations. A detailed investigation of the Raman effect in crystalline benzil does not appear to have been made. The dynamic X-ray reflections of benzil have been studied thorow by Mrs. Lonsdale (1942) and also by R. V. Subrahmanian (1942). A careful inspection of these photographs will, no doubt, throw considerable light on the orientations of the benzene rings in the crystal.

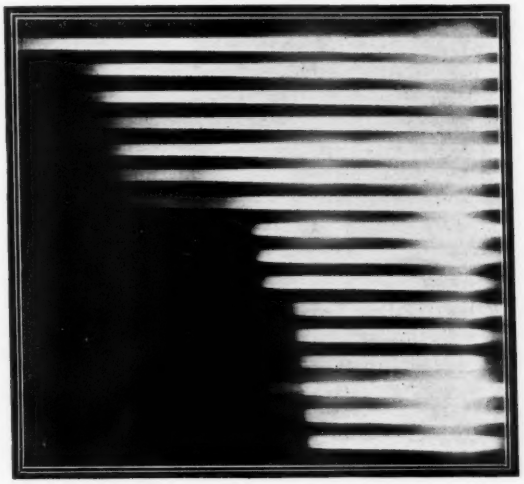
But this still leaves the question about the origin of the optical rotatory power of benzil unanswered. A more detailed knowledge of the structure of the benzil molecule and crystal is certainly necessary before we can proceed to a deeper analysis of this aspect of the problem.

In conclusion, I express my sincere thanks to Prof. Sir C. V. Raman for the valuable suggestions he gave me during the course of this work.

8. SUMMARY

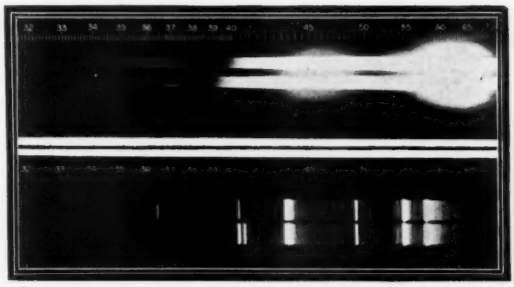
The paper reports a study of the rotatory dispersion and the ultraviolet absorption spectrum of crystalline benzil. Transmission spectra have been photographed with varying thicknesses of the crystal. Even with the thinnest specimens (0·02 mm.) there is an almost complete cut off in the transmitted intensity beyond 3400 Å marking the presence of an intense absorption band farther out in the ultraviolet. There is another comparatively feeble absorption which extends from 4500 Å onwards into the shorter wavelength region of the spectrum with a maximum at 3900 Å. This band is markedly pleochroic. The rotatory dispersion has been measured from 9000 Å in the

FIG. 1



Transmission by various thicknesses of crystalline benzil

FIG. 2



Photographs showing pleochroism in benzil. Thickness of crystal about 0·05 mm.

infrared upto 3600 Å in the ultraviolet right through the absorption band. A specimen of 0·03 mm. thick had to be used in order to penetrate the band. The crystal exhibits anomalous rotatory dispersion in the region of absorption. The one-term rotatory dispersion formula

$$\rho^2 = 6{\cdot}27\,\lambda^2/[\lambda^2 - (0{\cdot}24)^2]^2$$

fits the data quite well except in the immediate vicinity of the absorption band. The temperature variation of the rotatory power has been measured for three wavelengths in the visible. The rotatory power decreases slightly when the crystal is heated. Dispersion formulæ have been proposed in terms of observed absorption frequencies which give a satisfactory explanation for the interesting fact that the crystal, which is uniaxial and positive for λ 5893 A, becomes optically isotropic at λ 4205 Å.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XLIII. Preparation of 3-Hydroxy Flavanones

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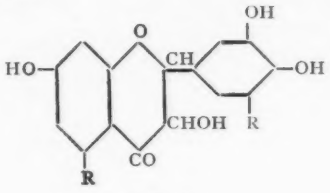
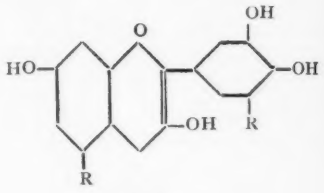
Several members of the new group of 3-hydroxy flavanones also called flavanolones have been recently discovered mainly in heartwoods. From the point of view of biogenesis they seem to occupy an important place in the evolution of anthoxanthins. They may be considered to be hydrated flavones or hydrogenated flavonols or hydroxylated flavanones. Actually they are accompanied by related members of the flavonol group in the plant sources, *e.g.*, fustin (I) is accompanied by fisetin (II) in the wood of *Rhus succedanea*;[1] ampelopsin (III) by myricetin (IV) in *Ampelopsis meliæfolia*.[2] Further the conversion of the flavanolones or their methyl ethers into the corresponding flavonols by dehydrogenation has been reported by several workers.[3, 4]



I, R=H
III, R=OH



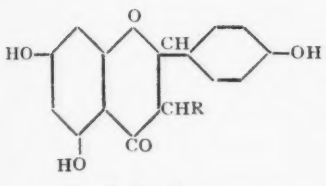
II, R=H
IV, R=OH

Among methods investigated in the past for the synthesis of 3-hydroxy flavanones, the most convenient would appear to be the bromination of the corresponding flavanones which is found to take place in the 3-position and subsequent exchange of the bromine atom for an acetate and eventually a hydroxyl group. Zemplen and Bognar[5] employed the acetate of hydroxy flavanones which were brominated in presence of ultra-violet light to yield 3-bromo flavanones. Earlier Kostanecki[6] used the flavanone methyl ether; in this case chances of nuclear bromination cannot altogether be avoided. A more readily available method for the synthesis of this important group

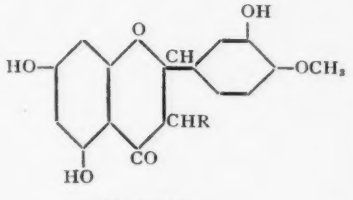
of compounds seemed to be desirable and hence the work reported in this communication.

In an earlier publication[7] on a new synthesis of flavones we employed the combined action of iodine and sodium acetate in alcoholic solution on a number of flavanones and this provided a convenient method of synthesis of flavones containing a hydroxyl in the 5-position. If however, instead of using sodium acetate, silver acetate is employed, the intermediate stages originally postulated for the iodine oxidation can be obtained. 3-Hydroxy flavanones constitute the important products in certain cases and their transformations can be studied (see Seshadri[8]). However there are differences in the course of the reaction depending upon the nature of the flavanone used as the starting material. Typical examples are discussed in the following paras.

Naringenin (V) and hesperetin (VI) are polyhydroxy flavanones and have been chosen first for the present study. They yield 3-acetoxy compounds by the action of iodine and silver acetate and these can be hydrolysed to the 3-hydroxy compounds. Among these products 3-hydroxy naringenin (V *a*), has been reported as a natural product.[3] But the synthetic compound differs from the natural one in its properties because the former is necessarily racemic and the latter optically active. 3-Hydroxy-hesperetin (VI *a*) has earlier been prepared by Zemplen and Bognar[5] using the 3-bromo compound as an intermediate and there is fair agreement between their product and ours.



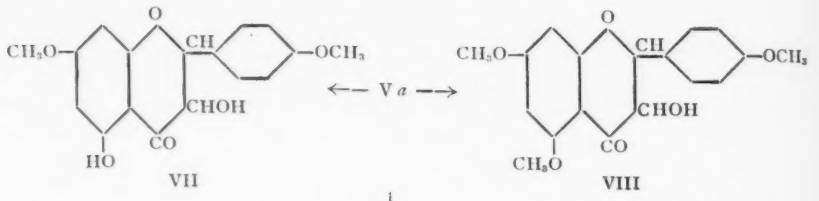
V, R=H
V *a*, R=OH



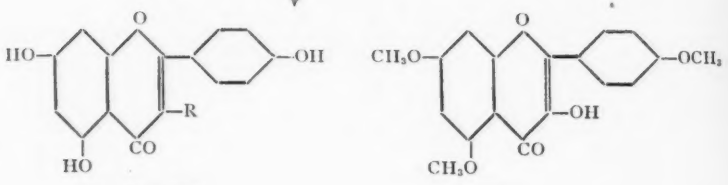
VI, R=H
VI *a*, R=OH

Besides optical activity there seems to be considerable difference between natural and synthetic compounds in their action towards alcoholic sulphuric acid. Using a natural sample of 3-hydroxy naringenin provided by Dr. Pew and isolated from the bark of Douglas fir wood[3] it has now been possible to prepare its dimethyl (VII) and trimethyl (VIII) ethers. The latter underwent dehydrogenation in acid solution to yield kæmpferol 5:7:4′-trimethyl ether (IX) whose properties agreed with the records found in the literature.[9] Pew reported similar dehydrogenation of the natural 3-hydroxy naringenin

in 2 normal sulphuric acid when a current of air was passed.[3] On the other hand synthetic 3-hydroxy naringenin underwent only dehydration under the same experimental conditions giving rise to apigenin (X *b*). The dehydration could be effected by simply refluxing with 4% alcoholic sulphuric acid for 24 hours.



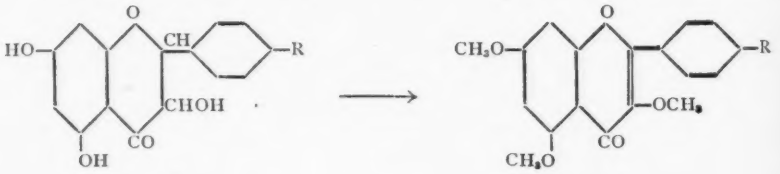
VII ⟵ V *a* ⟶ VIII



X *a*, R=OH
X *b*, R=H

IX

There seems to be, however, agreement in the behaviour of the natural and synthetic 3-hydroxy flavanones towards methylating agents. Complete methylation of pinobanksin (XI) by Lindstedt using excess of methyl sulphate and anhydrous potassium carbonate in acetone solution was reported to be accompanied by dehydrogenation yielding galangin trimethyl ether (XII) in low yield.[10] Synthetic 3-hydroxy-naringenin (V*a*) has now been found to behave similarly and give a small yield of O-tetramethyl kæmpferol (XIII). Dehydrogenation seems to be the earlier stage and the methylation of the 3-hydroxyl group (enol) a later stage since otherwise the secondary alcoholic hydroxyl group of the flavanonols would be unaffected. This has been

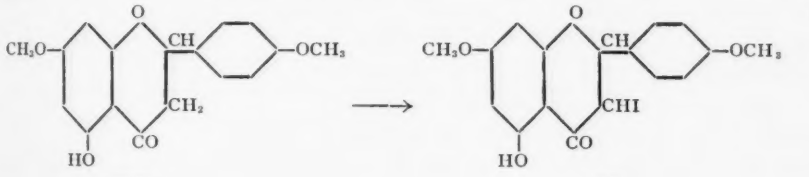


XI, R=H
V *a*, R=OH

XII, R=H
XIII, R=OCH_3

confirmed by boiling the natural 3-hydroxy naringenin (V*a*) with anhydrous potassium carbonate alone in acetone solution omitting dimethyl sulphate when kæmpferol (X *a*) could be obtained as the product.

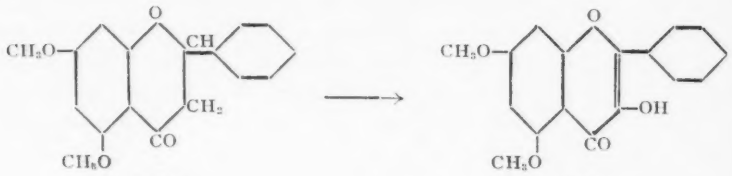
An interesting result has been obtained in the reaction of naringenin 7:4′-dimethyl ether (XIV) which has only one free hydroxyl group in the 5-position; the product obtained on heating an alcoholic solution of the compound with iodine and silver acetate is found to be a mono iodo compound. This should be the 3-iodo compound (XV) the intermediate postulated in the mechanism of iodine oxidation;[7] the reaction stops here. However, when the iodo compound is refluxed in acetic anhydride solution with silver acetate it forms 3:5-diacetoxy-7:4′-dimethoxy flavanone (XVI). It could not be successfully crystallised and was therefore directly refluxed for 20 hours with alcoholic sulphuric acid. It underwent simultaneous hydrolysis and dehydration yielding apigenin dimethyl ether (XVII). This seems to be the first example of successful iodination of the 3-position of a flavanone ring using iodine and silver acetate. The 3-iodo compound on treatment with aqueous sodium hydroxide or alcoholic sodium acetate gave apigenin 7:4′-dimethyl ether (XVII).



XIV XV XVII XVI

5:7-Dimethoxy flavanone (XVIII) having no free hydroxyl groups gave different results when subjected to the same course of reactions. This also formed a 3-iodo derivative as the first stage. But when it was boiled with alcoholic potassium hydroxide for five minutes the resulting compound was found to be soluble in aqueous alkali, and acidification of the alkali

solution yielded a bright yellow compound. It gave a deep reddish brown colour with ferric chloride and melted at 178–80° and thus agreed with the description of 5: 7-dimethoxy-3-hydroxy flavone (XIX) described in the literature.[11] Acetylation yielded an acetate also agreeing with the earlier description.[11] The 3-iodo flavanone could be converted into the corresponding 3-acetoxy derivative by refluxing with acetic anhydride and silver acetate. Attempts to deacetylate this product using alcoholic potash (2%) yielded only the alkali-soluble galangin dimethyl ether (XIX) identical with the one obtained directly from the 3-iodo-compound. This is rather remarkable and is explicable on the basis that the 3-hydroxy compound which may be formed first undergoes ready dehydrogenation in alkaline medium. Such dehydrogenations are recorded in earlier literature also.[14]



XVIII XIX

EXPERIMENTAL

3-*Acetoxy hesperetin*

Hesperetin required for this purpose was obtained using the method of Gupta *et al.*[12]

Hesperetin (1 g.) was dissolved in absolute alcohol (25 c.c.) and pure powdered silver acetate (1·5 g.) added to it. The mixture was boiled and a boiling solution of iodine in absolute alcohol (0·85 g. in 20 c.c.) added to it. After refluxing for 4 hours it was filtered, the silver salts washed with hot alcohol and alcohol distilled off from the filtrate. The oily residue which solidified on cooling was twice crystallised from ethyl acetate-petrol mixture. It was obtained in the form of aggregates of pale yellow tiny prisms melting at 146–47°. It gave a violet colour with ferric chloride (Found: C, 58·9; H, 4·4; $C_{18}H_{16}O_8$, $\frac{1}{2}$ H_2O requires C, 58·5; H, 4·6%). Yield 0·6 g.

3-*Hydroxy-hesperetin* (*VI a*)

The 3-acetoxy compound (0·5 g.) given above was treated with aqueous sodium hydroxide (10 c.c., 2%) and the solution warmed on a water-bath for five minutes, cooled and acidified with ice-cold hydrochloric acid. The sticky mass that separated was filtered and washed with water. It was crystallised from boiling aqueous alcohol when it separated as tiny prisms

melting at 214–16° (Zemplen and Bognar[8] reported the m.p. as 202°). Yield of the pure product was 0·32 g. (70%). It gave a violet colour with ferric chloride and was easily soluble in aqueous sodium carbonate. Its alcoholic solution gave a brilliant red colour with magnesium and hydrochloric acid and a pink colour with zinc and hydrochloric acid (Found: C, 58·9; H, 4·4; $C_{16}H_{14}O_7$, $\frac{1}{2}$ H_2O requires C, 58·7; H, 4·6%).

3-Hydroxy naringenin (*V a*)

A mixture of naringenin (1 g.) and silver acetate (1·2 g.) in boiling absolute alcohol (20 c.c.) was treated with a boiling solution of iodine in the same solvent (0·85 g. in 20 c.c.) and the mixture refluxed for 4 hours. The product was worked up as in a previous experiment. 3-Acetoxy naringenin crystallised from dilute alcohol in the form of colourless tiny prisms melting at 226–28° (decomp.); yield 0·6 g. It gave a bright scarlet colour when treated with magnesium and hydrochloric acid and a pink colour with zinc dust and hydrochloric acid in alcoholic solution.

3-Acetoxy naringenin (0·25 g.) was hydrolyzed with aqueous sodium hydroxide (10 c.c., 2%) under mild conditions as described in the earlier experiment. It crystallised from boiling aqueous alcohol as almost colourless stout prisms melting at 238–40° (decomp.) with darkening at 230°; yield 0·16 g. Its alcoholic solution developed a reddish violet colour with ferric chloride, a scarlet red colour with magnesium and hydrochloric acid and a pink colour with zinc and hydrochloric acid. It thus agreed in its reactions with those described for 3-hydroxy naringenin. However the mixed melting point with the natural sample supplied by Dr. Pew was considerably depressed because they were different stereo isomers (Found: C, 58·9; H, 4·5; $C_{15}H_{12}O_6$, H_2O requires C, 58·8; H, 4·6%).

Methylation of 3-hydroxy naringenin

(*a*) *Synthetic sample to kæmpferol tetramethyl ether* (*XIII*)

3-Hydroxy naringenin (0·5 g.) was refluxed in dry acetone solution (200 c.c.) with dimethyl sulphate (0·7 c.c., excess) and anhydrous potassium carbonate (2 g.) for 24 hours. The mixture was filtered, the potassium salts washed with hot acetone and the solvent removed by distillation. The oily mass solidified on keeping with a little alcohol for a few days in the refrigerator. It was filtered and crystallised thrice from alcohol when it was obtained as colourless needles melting at 164–65°. Further crystallisation did not raise the melting point. It gave no colour with ferric chloride, was insoluble in aqueous alkali and developed a bright red colour when its alcoholic solution was treated with magnesium and hydrochloric acid. It

agreed in its properties and reactions with kæmpferol tetramethyl ether and a mixed melting point with an authentic sample was undepressed (Found: C, 66·2; H, 5·5; $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·5%).

(*b*) *Natural Sample :* (i) 7 : 4′-*Dimethyl ether* (*VII*).—3-Hydroxy naringenin (0·3 g.) kindly supplied by Dr. Pew was dissolved in dry acetone (20 c.c.), dimethyl sulphate (0·22 c.c., 2 moles) and anhydrous potassium carbonate (0·5 g.) added and the mixture refluxed for 6 hours. On filtering and distilling off acetone from the filtrate, a colourless crystalline solid was obtained. It crystallised from alcohol as colourless clusters of needles melting at 189–90°. It gave a red colour with ferric chloride, a bright red colour with magnesium and hydrochloric acid and a pink colour with zinc dust and hydrochloric acid. It was sparingly soluble in aqueous alkali, the solution developing a yellow colour gradually (Found: C, 64·1; H, 5·0; $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1%).

(ii) 5 : 7 : 4′-*Trimethyl ether* (*VIII*).—The natural sample of 3-hydroxy naringenin (0·3 g.) was methylated with 3 moles of dimethyl sulphate (0·33 c.c.) by refluxing in acetone solution with anhydrous potassium carbonate (1 g.) for 10 hours. The methylated product crystallised from alcohol as aggregates of colourless rectangular tablets melting at 142–43°. It gave no colour with ferric chloride in alcohol and was insoluble in dilute aqueous alkali (Found: C, 64·0; H, 6·0; loss on drying 2·7; $C_{18}H_{18}O_6$, $\frac{1}{2}H_2O$ requires C, 63·7; H, 5·7%; loss on drying 2·5%). It thus agreed in its properties with 5 : 7 : 4′-trimethoxy-3-hydroxy flavanone.

Conversion to kæmpferol 5 : 7 : 4′-*trimethyl ether* (*IX*)

The above methylation product (trimethyl ether) (0·15 g.) was refluxed with alcoholic sulphuric acid (20 c.c., 4%) for 25 hours on a water-bath. It was concentrated to 10 c.c. under reduced pressure and diluted with an equal volume of water. The yellow solid that separated was filtered and crystallised from alcohol. It formed yellow needles melting at 149–50°. It gave a deep brown colour with ferric chloride and was soluble in aqueous alkali giving a yellow solution. With concentrated sulphuric acid it gave a greenish yellow fluorescence (Found: C, 62·5; H, 5·5; $C_{18}H_{16}O_6$, H_2O requires C, 62·4; H, 5·2%). Kostanecki and Tambor[9] reported earlier this compound as a monohydrate and gave m.p. 149–50°.

Conversion of natural sample to kæmpferol (*X a*)

The natural sample of 3-hydroxy naringenin was refluxed in acetone solution in the presence of anhydrous potassium carbonate for 16 hours when the solution gradually turned yellow. It was then filtered and acetone

removed by distillation. The yellow solid when crystallised from alcohol was found to be a mixture (m.p. 210–20°) and crystallisation did not effect a separation. The mixture developed a greenish yellow fluorescence with concentrated sulphuric acid thus showing the presence of kæmpferol, the original compound gave only a bright yellow solution. Paper chromatography using phenol saturated with water as the irrigating solvent gave a bright yellow ring corresponding to kæmpferol (circular Rf. at 0·78) compared with the ring developed by an authentic specimen.[13]

Iodination of naringenin 7:4′-dimethyl ether to 3-iodo naringenin dimethyl ether (XV)

Naringenin 7:4′-dimethyl ether (1 g.) was refluxed in absolute alcoholic solution with iodine (0·8 g. in alcohol 20 c.c.) and silver acetate (2 g.) for 4 hours. The mixture was then filtered, alcohol distilled off from the filtrate and the colourless solid twice crystallised from alcohol. It was obtained as colourless long prisms and prismatic needles melting at 164–66°. It gave a positive test for iodine. It gave a red colour with ferric chloride and was sparingly soluble in alkali (Found: C, 47·6; H, 3·9; $C_{17}H_{15}O_5I$ requires C, 47·9; H, 3·5%).

Conversion to apigenin dimethyl ether (XVII)

(i) The above iodo compound (0·1 g.) was heated on a water-bath with aqueous alcoholic sodium hydroxide (4 c.c., 2%) for 10 minutes. The mixture was then diluted and acidified with dilute hydrochloric acid. The product crystallised from alcohol as almost colourless needles melting at 170–71° identical with apigenin 7:4′-dimethyl ether. Yield 0·06 g. On acetylation using acetic anhydride and pyridine it yielded the acetate which crystallised from alcohol as colourless prismatic needles melting at 193–4° identical with the 5-acetate of apigenin 7:4′-dimethyl ether.

(ii) The 3-iodo compound (0·1 g.) was heated with acetic anhydride (5 c.c.) and silver acetate (0·2 g.) at 140° for 8 hours. The silver salts were separated by filtration and the acetic anhydride decomposed by putting in ice pieces and leaving overnight. Water was then decanted off and the sticky mass washed with water twice by decantation. Attempts to crystallise it were not successful and hence it was directly used for further reaction.

It was refluxed with alcoholic sulphuric acid (4%) for 16 hours, and the alcoholic solution was then concentrated under reduced pressure. The solid that separated on cooling, when recrystallised from alcohol melted at 170–71° agreeing with apigenin dimethyl ether and also gave an acetate

identical with 5-acetoxy 7: 4′-dimethoxy flavone (m.p. and mixed m.p. 193–94°).

(iii) The 3-iodo compound was boiled with sodium acetate (1 g.) in alcoholic solution (50 c.c.). Even from the boiling solution a yellow crystalline substance separated. It was filtered and washed with hot alcohol. It appeared as yellow needles melting at 260–61°. The alcoholic filtrate on complete removal of the solvent gave a little of a pale yellow solid. On recrystallisation from the minimum amount of alcohol it melted at 170–71° and was identical with apigenin dimethyl ether.

Iodination of 5: 7-*dimethoxy flavanone to* 3-*iodo*-5: 7-*dimethoxy flavanone*

To a boiling absolute alcoholic solution of 5: 7-dimethoxy flavanone (1 g. in 20 c.c.) was added silver acetate (1·5 g.) and a boiling solution of iodine (0·8 g.) in the same solvent. The colour of iodine gradually disappeared in the course of 30 minutes. The mixture was refluxed for 4 hours, then filtered and alcohol distilled from the filtrate. The colourless residue when crystallised from excess of alcohol separated as colourless needles melting at 183–84°. It gave no colour with ferric chloride and was insoluble in aqueous alkali (Found: C, 49·6; H, 4·0; $C_{17}H_{15}O_4I$ requires C, 49·8; H, 3·7%).

Conversion to galangin-5: 7-*dimethyl ether* (*XIX*)

The 3-iodo compound (0·2 g.) was heated on a water-bath with absolute alcoholic potash (6 c.c., 4%) for 10 minutes, alcohol removed under reduced pressure, the residue dissolved in water and the solution acidified after cooling. The yellow solid was collected, washed with water and crystallised from alcohol. It was obtained as yellow prisms melting at 178–80°; it gave a deep reddish brown colour with ferric chloride and was soluble in aqueous alkali. It thus agreed with the properties of galangin 5: 7-dimethyl ether described in literature.[11]

Its acetate prepared by heating it with acetic anhydride and pyridine crystallised from alcohol as colourless stout rectangular prisms melting at 184–86°. It agreed with the description of 3-acetoxy 5: 7-dimethoxy flavone found in literature.[11]

SUMMARY

The action of iodine and silver acetate varies with the type of flavanones employed, and yields the intermediate stages postulated in the new flavone synthesis using iodine and sodium acetate. The polyhydroxyflavanones, naringenin and hesperetin form directly the 3-acetates which can be hydrolysed to the 3-hydroxy compounds. On the other hand from naringenin

7:4′-dimethyl ether and 5:7-dimethoxy flavanone, the 3-iodo compounds can be isolated as the first intermediates. The behaviour of the 3-hydroxy flavanones in acid and alkaline conditions also varies; either dehydrogenation to flavonol or dehydration to flavone taking place.

Our thanks are due to Dr. Pew of the Forest Products Laboratory, Madison, U.S.A., for the generous supply of 3-hydroxy naringenin used in this work.

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